FULL PAPER

σ*-Aromaticity in Three-Membered Rings

Andreas Göller[1] and Tim Clark[2]

[1]Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Lessingstraße 10, D-07743 Jena, Germany.
E-mail: goeller@pc04.chemie.uni-jena.de

[2]Computer Chemie Centrum, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25, D-91052 Erlangen, Germany

Abstract The structures and energies of unsaturated three-membered rings of the general formula $(CH)_2XY_n^m$, with charge = m and n substituents Y at X (Y = fluorine, chlorine, bromine, hydrogen, X = phosphorus, silicon, nitrogen, carbon) are compared to their saturated analogs. The structures were optimized with B3LYP/6-311+G(2d,p) and at MP2/6-31+G(d), with single point energy calculations on the latter geometries at MP4SDTQ/6-31+G(d).
The geometrical changes in bond lengths and angles, which correlate with substituent electronegativities, are discussed for the different ring systems. The relative stabilities of unsaturated and saturated rings are compared using isodesmic ring-opening reactions and homodesmic substituent-exchange reactions. σ*-Aromaticity, a hyperconjugative effect found in the disubstituted rings, causes lowering of ring strain energies for the unsaturated rings and preference of unsaturated rings over saturated ones for the more electronegative substituents. For the mono-substituted π-aromatic silacyclopropenes and cyclopropenes, a destabilization by more electronegative ligands is found. For the neutral rings mono-substituted at main group V atoms like the 1*H*-phosphirenes and also the isoelectronic negatively charged rings with main group IV atoms like the silacyclopropenium anions, no correlation of stabilization energies or geometrical changes with ligand electronegativity is found.

Keywords σ*-aromaticity, Hyperconjugation, *ab initio* calculations, Phosphorus rings, Weak interactions

Introduction

Three-membered rings have drawn the interest of experimental [1] and theoretical chemists [2] for many decades.

The stability and reactivity of these species is dictated by an interplay of steric and electronic influences. In detail these are the bonding situation in the ring, the substitution pattern of the heavy atoms in the ring and the molecular charge. These can give rise to aromatic stabilization or antiaromatic destabilization as well as inductive, mesomeric and hyperconjugative effects.

In the past we have focussed on the unsaturated three-membered phosphorus rings, especially the phosphorenylium cation **1**, the phosphirenes [3] **2**, and the 1*H*-phosphirenium cations [4] **3** (Scheme 1). Not much is known about cation

---

Correspondence to: A. Göller

Scheme 1 *Unsaturated three-membered phosphorus rings: phosphorenylium cation **1**, 1H-phosphirene **2**, 1H-phosphirenium cations **3** and 1H-phosphiranium cation **4***

1   **2**   **3**   **4**
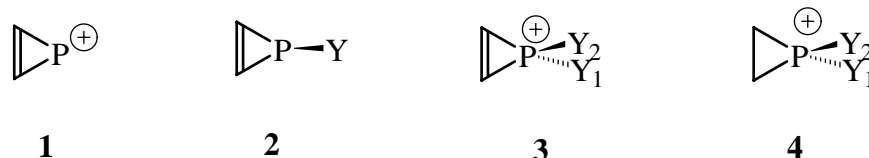
Scheme 2 *Fluoro-disubstituted cyclopropene is stabilized and cyclopentadiene destabilized by hyperconjugation relative to the hydrogen-disubstituted rings; energies in kJ mol⁻¹ [13]*

-40.1

$+58.9$
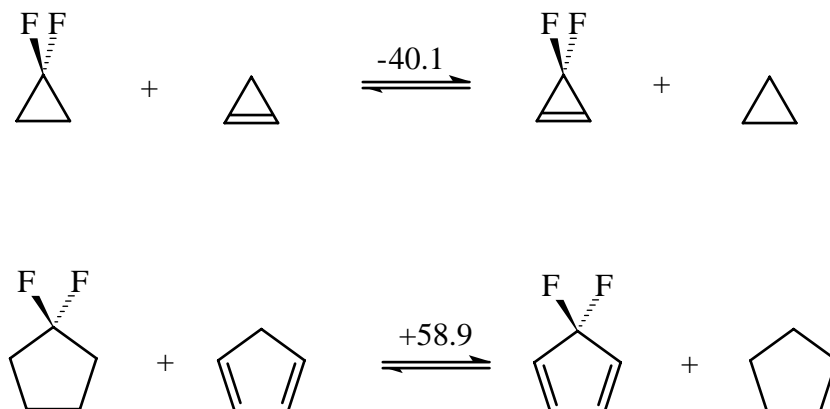
1. It is the lowest energy conformer on the $C_2H_2P^+$ energy surface [5]. It was first synthesized in 1994 [6] in liquid SO_2 and discussed [7] as an intermediate in the nucleophilic substitution of **2**. Cation **1** is isoelectronic with the cyclopropenium cation and should therefore be aromatic, as calculations indicate [8]. The 1*H*-phosphirenium cations **3**, on the other hand, were found [9] to show a special hyperconjugative effect, σ*-aromaticity, which stabilizes the phosphirenium cations as well as silacyclopropenes compared

to their saturated analogs. The phosphirenes **2** should exhibit no stabilization and behave similarly to their saturated counterparts.

Hockless et al. [10] synthesized the *1H*-phosphirenium cations **3** by exchange of the saturated C_2-moiety in phosphiranium cations **4** by an unsaturated one, which is an indication of an excess σ*-aromatic stabilization in unsaturated rings. This effect has been demonstrated by comparing the dihydrogen-rings with their halogen disubstituted coun-

Figure 1 *Stabilizing interaction of the double bond π-MO with the σ*-MO formed by the p_z orbital at atom X and the p_x-orbitals at ligands Y (X = P, Si, N, C; Y = F, Cl, Br, H)*

π   σ

σ*
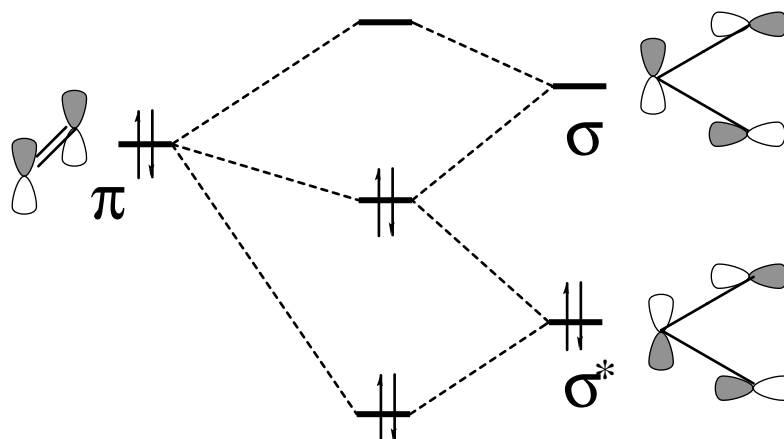
Scheme 3 *Three-dimensional representations; X = P, Si, N, C; Y = F, Cl, Br, H*
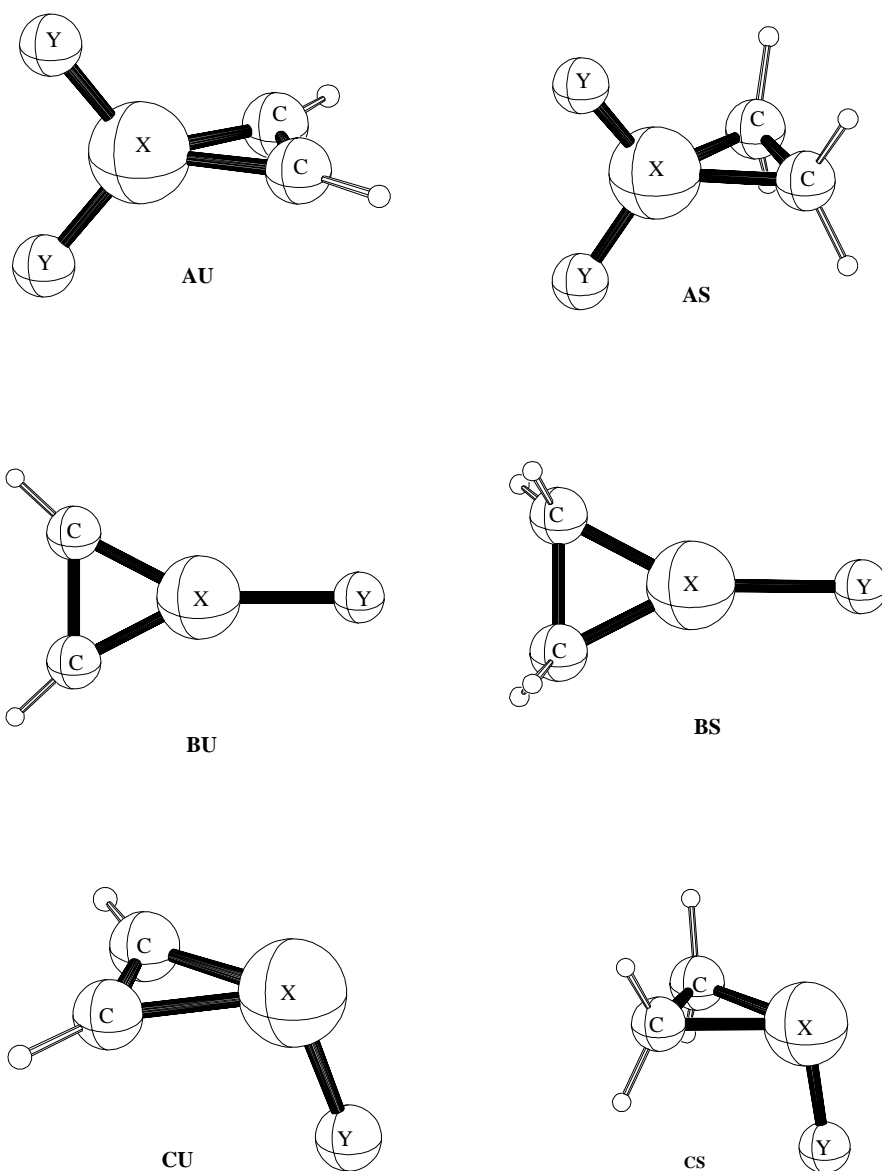
terparts. There is now convincing evidence, both computationally [11a] and experimentally [11b], for negative hyperconjugation by C-F σ^*-orbitals overlapping with unshared electron pairs from adjacent carbons. The halogen exchange reaction of 1,1-difluorocyclopropane with cyclopropene (Scheme 2) is therefore exothermic by 40.1 kJ mol^{-1} and 1,1-difluorocyclopropene, [12,13] has been suggested to be aromatic to a certain degree, whereas the analogous reaction for the cyclopentadienes is endothermic by 58.9 kJ mol^{-1}.

σ^*-Aromaticity, as defined [9], is conjugation of the double bond fragment with the empty low-lying σ^*-orbital consisting of the ligand p_z-orbitals and the p_x-orbital of phosphorus, as shown in Figure 1. This σ^*-orbital is of the appropriate symmetry to give a delocalized 3c-2e-interaction and an excess stabilization similar to that of the π-aromatic cyclopropenium cation. This effect is larger for more electronegative ligands at phosphorus, which lower the σ^*-orbital more effectively, and is only found for the unsaturated rings. The geometric consequences are an elongation of the CC double bond and a shortening of the CP single bonds.

In this work, we discuss the σ^*-aromaticity of disubstituted unsaturated (U) σ^*-aromatic compounds of general type **AU** (Scheme 3) relative to the disubstituted saturated (S) rings **AS**, and we extend the results published earlier [9] to the disubstituted azirines and the cyclopropenes. We compare to the π-aromatic cyclopropenium and silacyclopropenium cations **BU** and their saturated analogs **BS**, which show contrary

Table 1a *Bond lengths and angles for the structures of types* **AU** *and* **AS** *(see Scheme 3)*

Y	method	AU				AS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
phosphorus									
F	HF [a]	168.8	138.0	48.27	102.77	172.5	161.8	55.13	107.33
	MP2 [b]	169.0	138.1	48.20	102.73	173.3	163.1	55.90	106.37
	B3 [c]	168.6	136.4	47.71	102.41	172.9	164.3	56.74	106.56
Cl	HF	170.5	132.8	45.05	108.55	176.8	156.2	52.78	113.18
	MP2	172.3	135.6	46.34	109.16	177.0	157.3	52.42	112.33
	B3	172.1	134.1	45.85	108.59	177.2	158.1	53.00	112.34
Br	HF	172.7	132.9	45.27	109.21	179.5	154.5	51.84	114.88
	MP2	173.5	135.2	45.85	110.55	178.4	156.0	50.95	113.76
	B3	173.2	132.5	45.36	110.07	178.5	156.8	52.11	114.02
H	HF	173.9	130.5	44.06	111.25	180.3	151.6	49.81	115.38
	MP2	176.0	132.7	44.28	112.64	180.5	152.1	49.72	114.35
	B3	175.8	131.2	43.83	112.29	180.7	152.4	49.88	114.60
Δ [d]	HF	-5.1	7.5	4.21	-8.48	-7.8	10.2	5.32	-8.05
	MP2	-7.0	5.4	3.92	-9.91	-7.2	11.0	6.18	-7.98
	B3	-7.2	5.2	3.88	-9.88	-7.8	11.9	6.86	-8.04

[a] HF = HF/6-31G(d)
[b] MP2 = MP2/6-31+G(d)

[c] B3 = B3LYP/6-311+G(2d,p)
[d] Δ is the difference between the value for Y = F and Y = H

Table 1b *Bond lengths and angles for the structures of types* **AU** *and* **AS** *(see Scheme 3)*

Y	method	AU				AS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
silicon									
F	HF [a]	175.4	135.2	45.33	103.67	180.1	162.1	53.48	106.87
	MP2 [b]	177.2	138.0	45.84	103.23	181.1	162.4	53.30	107.50
	B3 [c]	176.7	136.2	45.36	103.71	180.3	163.4	53.91	107.09
Cl	HF	176.7	134.3	44.67	107.73	181.7	159.3	51.99	110.38
	MP2	178.5	136.8	45.06	106.61	182.6	159.5	51.82	111.51
	B3	178.0	135.1	44.60	106.96	182.0	160.2	52.22	110.53
Br	HF	178.4	134.5	44.29	108.34	183.5	158.2	51.06	111.10
	MP2	179.0	136.6	44.87	106.89	183.3	158.5	51.09	112.48
	B3	178.5	134.8	44.38	107.67	182.7	159.5	51.77	111.41
H	HF	180.2	132.6	43.17	111.49	185.1	155.5	49.66	113.56
	MP2	182.2	134.7	43.37	109.71	186.2	154.9	49.14	115.12
	B3	181.8	133.0	42.91	111.49	185.8	155.3	49.42	114.60
Δ [d]	HF	-4.8	2.6	2.16	-7.82	-5.0	6.6	3.82	-6.69
	MP2	-5.0	3.3	2.47	-6.48	-5.1	7.5	4.16	-7.62
	B3	-5.1	3.2	2.45	-7.78	-5.5	8.1	4.49	-7.51

[a] HF = HF/6-31G(d)
[b] MP2 = MP2/6-31+G(d)

[c] B3 = B3LYP/6-311+G(2d,p)
*[d] Δ is the difference between the value for Y = F and Y = H*

Table 1c *Bond lengths and angles for the structures of types* **AU** *and* **AS** *(see Scheme 3)*

Y	method	AU				AS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
nitrogen									
F	HF [a]	140.7	128.0	54.10	106.20	146.2	149.2	61.33	109.38
	MP2 [b]	140.2	132.4	56.34	104.25	146.3	152.0	62.60	108.91
	B3 [c]	140.9	130.2	55.06	104.93	147.0	151.6	62.05	108.89
Cl	HF	145.6	126.4	51.39	112.54	149.9	146.6	58.57	114.00
	MP2	146.0	130.2	52.99	111.69	150.1	148.9	59.49	113.89
	B3	144.8	128.6	52.72	111.05	150.2	148.8	59.41	113.80
Br	HF	146.0	127.0	51.54	113.28	149.7	146.6	58.62	114.41
	MP2	146.2	130.3	52.95	112.06	150.4	148.9	59.34	114.27
	B3	144.7	128.5	52.71	111.85	149.9	148.8	59.48	114.33
H	HF	148.5	125.5	49.99	114.16	148.8	146.0	58.77	113.10
	MP2	150.1	128.6	50.75	114.89	149.8	147.6	59.05	113.73
	B3	150.2	126.8	49.97	114.87	150.1	147.4	58.82	113.82
Δ [d]	HF	-7.8	2.5	4.11	-7.96	-2.6	3.2	2.56	0.51
	MP2	-9.9	3.8	5.59	-10.64	-3.5	4.4	3.55	-4.82
	B3	-9.3	3.4	5.09	-9.94	-3.1	4.2	3.23	-4.93

[a] HF = HF/6-31G(d)   *[c] B3 = B3LYP/6-311+G(2d,p)*
[b] MP2 = MP2/6-31+G(d)   *[d] Δ is the difference between the value for Y = F and Y = H*

Table 1d *Bond lengths and angles for the structures of types* **AU** *and* **AS** *(see Scheme 3)*

Y	method	AU				AS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
carbon									
F	HF [a]	143.4	129.9	53.86	105.71	146.5	153.6	63.23	109.36
	MP2 [b]	144.2	132.2	55.01	105.54	147.1	155.1	63.62	109.26
	B3 [c]	144.3	131.3	54.14	105.78	147.3	155.0	63.45	109.13
Cl	HF	144.7	128.7	52.82	109.44	148.6	150.7	60.93	112.78
	MP2	146.1	131.9	53.68	109.98	149.2	152.1	61.26	113.05
	B3	145.1	130.3	53.35	109.13	149.0	152.3	61.45	112.45
Br	HF	145.3	129.4	52.91	110.00	149.3	150.7	60.61	113.28
	MP2	146.0	132.1	53.79	110.23	149.6	152.1	61.11	113.53
	B3	144.6	130.4	53.59	109.41	148.9	152.3	61.51	112.84
H	HF	149.5	127.6	50.52	112.92	149.7	149.7	60.00	114.25
	MP2	151.1	130.5	51.16	113.95	149.9	149.9	60.00	114.11
	B3	150.9	128.7	50.50	113.78	150.6	150.6	60.00	114.16
Δ [d]	HF	-6.1	2.3	3.34	-7.21	-3.2	3.9	3.23	-4.89
	MP2	-6.9	1.7	3.85	-8.41	-2.8	5.2	3.62	-4.85
	B3	-6.6	2.6	3.64	-8.00	-3.3	4.4	3.45	-5.03

[a] HF = HF/6-31G(d)   *[c] B3 = B3LYP/6-311+G(2d,p)*
[b] MP2 = MP2/6-31+G(d)   *[d] Δ is the difference between the value for Y = F and Y = H*
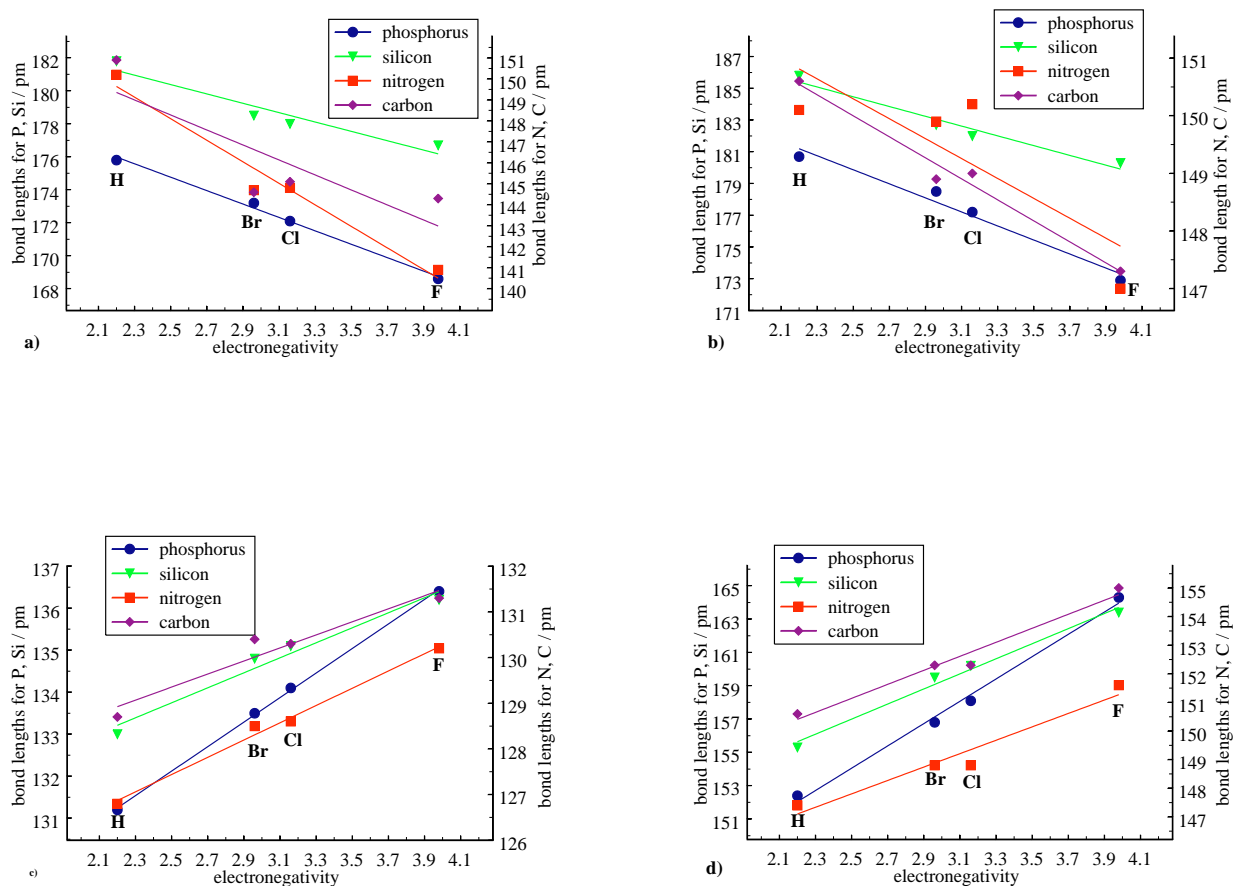
Figure 2 *Changes in bond lengths Δ_{CX} (2a, 2b) and Δ_{CC} (2c, 2d) for unsaturated (2a, 2c) and saturated (2b, 2d) rings AS and AU, B3LYP / 6-311+G(2d,p) optimized*

behavior, and to the non-aromatic monosubstituted rings **CU**, like 1*H*-phosphirenes **2**, and their saturated analogs **CS**, which, as neutral species, should not profit significantly from hyperconjugation [14]. The ring atoms X are always P, Si, N, C and the substituents Y are F, Cl, Br and H. We sort the substituents by the electronegativity scale of Pauling [15] and compare all stabilizing effects to the hydrogen-substituted case.

Computational methods

All calculations were performed with Gaussian94 [16]. The structures were first optimized using RHF/6-31G(d) [17], and then refined using second-order Møller-Plesset perturbation theory [18] with the frozen-core approximation and a diffuse-augmented basis set [19] (MP2/6-31+G(d)). The final energies were obtained by MP4SDTQ/6-31+G(d)//MP2/6-31+G(d) single point calculations. Additionally, nonlocal
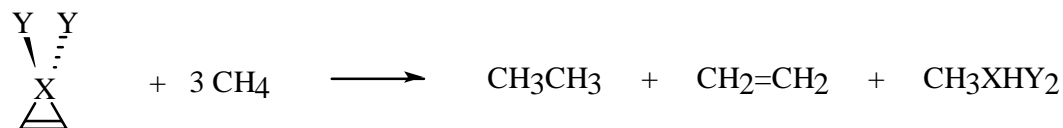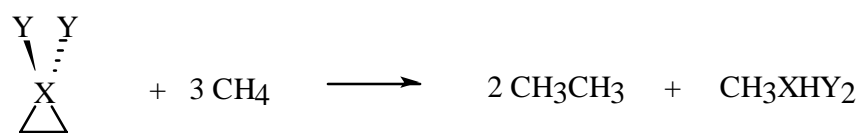
hybrid density functional theory calculations with B3LYP [20] (Becke3 exchange functional together with the Lee, Yang and Parr correlation functional) using the more extended 6-311+G(2d,p) basis set were also carried out. For bromine a split-valence basis by Schäfer, Horn and Ahlrichs [21] was used. The structures were characterized as minima at the RHF/6-31G(d) level of theory and the zero point energies calibrated with a factor of 0.89 [22].

We give all relative energies in units of kJ mol^{-1}, bond lengths in pm and angles in degrees.
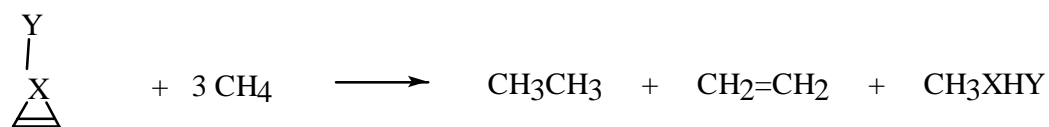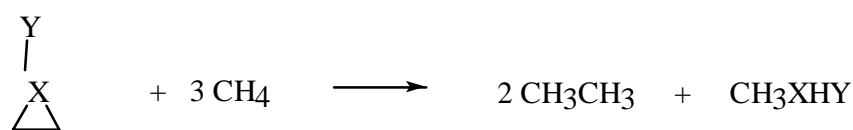
Results

σ*-aromatic compounds

Structures All structures discussed in this section have C$_{2v}$ symmetry, except for cyclopropane, which is D$_{3h}$ symmetric. We expect an elongation of the CC bond and a shortening of
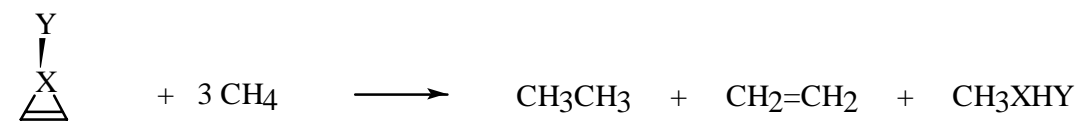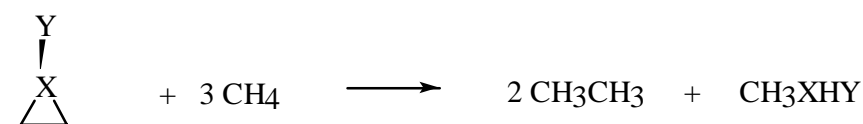
$$\text{(Y Y / X triangle)} + 3\,CH_4 \longrightarrow 2\,CH_3CH_3 + CH_3XHY_2$$

$$\text{(Y Y / X trapezoid)} + 3\,CH_4 \longrightarrow CH_3CH_3 + CH_2{=}CH_2 + CH_3XHY_2$$

X = P(+1), Si, N(+1), C

a)

$$\text{(Y / X triangle)} + 3\,CH_4 \longrightarrow 2\,CH_3CH_3 + CH_3XHY$$

$$\text{(Y / X trapezoid)} + 3\,CH_4 \longrightarrow CH_3CH_3 + CH_2{=}CH_2 + CH_3XHY$$

X = Si(+1), C(+1)

b)

$$\text{(Y / X triangle)} + 3\,CH_4 \longrightarrow 2\,CH_3CH_3 + CH_3XHY$$

$$\text{(Y / X trapezoid)} + 3\,CH_4 \longrightarrow CH_3CH_3 + CH_2{=}CH_2 + CH_3XHY$$

X = P, Si(-1), N, C(-1)

c)

Scheme 4 *Isodesmic reactions for determining the ring strain energy. Reactions (**a**) are defined for the σ*-aromatic compounds of type **A**, reactions (**b**) for the π-aromatic **B** and reactions (**c**) for the non-aromatic **C***

Table 2 *B3LYP/6-311+G(2d,p) calculated ring strain energies* $\Delta E = E_{saturated} - E_{unsaturated}$

Y	phosphorus			silicon			nitrogen			carbon		
	AU	**AS**	**ΔE**	**AU**	**AS**	**ΔE**	**AU**	**AS**	**ΔE**	**AU**	**AS**	**ΔE**
ΔE = AS - AU												
F	-145.7	-123.4	22.3	-131.1	-134.8	-3.8	-162.7	-80.9	81.8	-147.8	-96.8	51.1
Cl	-119.2	-93.9	25.3	-118.6	-118.8	-0.2	-161.7	-69.7	92.0	-138.9	-85.6	53.2
Br	-113.4	-85.4	28.1	-115.5	-113.3	2.2	-163.9	-72.1	91.8	-137.1	-85.2	51.3
H	-175.9	-74.7	41.2	-107.5	-98.5	9.0	-198.8	-68.1	130.8	-167.4	-77.0	90.4
ΔΔE [a]			18.9			12.8			49.0			39.3
	BU	**BS**	**ΔE**	**BU**	**BS**	**ΔE**	**BU**	**BS**	**ΔE**	**BU**	**BS**	**ΔE**
ΔE = BS - BU												
F				-141.3	-157.2	-15.9				-38.3	-120.9	-82.6
Cl				-117.2	-141.8	-24.6				-18.0	-98.9	-80.9
Br				-996.3	-1021.8	-25.6				-13.1	-95.4	-82.3
H				-910.4	-936.4	-43.6				+34.1	-109.6	-142.7
ΔΔE [a]						-27.7						-60.2
	CU	**CS**	**ΔE**	**CU**	**CS**	**ΔE**	**CU**	**CS**	**ΔE**	**CU**	**CS**	**ΔE**
ΔE = CS - CU												
F	-41.9	-29.3	12.6	-25.5	-28.8	-3.3	139.5	-71.9	67.6	-89.8	-37.2	52.7
Cl	-52.4	-31.4	21.0	-25.9	-30.5	-4.6	-159.8	-78.2	81.6			
Br	-53.6	-32.6	21.0	-23.3	-31.1	-7.9	-157.9	-79.5	78.4		-51.3	
H	-85.5	-40.4	46.1	-65.2	+19.3	84.6	-232.1	-86.4	145.7	-169.8	-52.2	117.6
ΔΔE [a]			33.5			87.9			78.1			64.9

[a] $\Delta\Delta E = \Delta E_{Y=H} - \Delta E_{Y=F}$.

the CX bond relative to the literature values [23] (given in pm) for non-constrained compounds:

C-P	184	C-Si	185
C-N	147	C-C	154
C=P	167	C=Si	172
C=N	128	C=C	134

The results for bond lengths CC and CX and the angles CXC and YXY, together with the changes of these values (Δ_{value} = value$_{hydrogen}$ - value$_{fluorine}$) are listed in Table 1. We will focus on the DFT values, for which we were able to use the most flexible basis set, since the results of MP2 calculations are quite similar except for the CC bond lengths, which are significantly longer for MP2 than for B3LYP. Hartree-Fock strongly underestimates the bond lengths. Some XC bond length deviations for brominated rings with X = P, Si, C are explained by the use of an ECP basis set for bromine.

The XC distances for MP2 and B3LYP are similar, the CC distances are significantly longer for MP2 than for B3LYP, which indicates the often found overestimation of correlation effects by MP2. In detail, the B3LYP calculated CC for the unsaturated species are 136.4 (F), 134.1 (Cl), 132.5 (Br) and 131.2 (H) pm for phosphorus with Δ_{CC} = 5.2 pm. Thus, we find an elongation of the double bond with more electronegative ligands Y and for Y = H, a short and localized CC double bond. For silicon the values are 136.2 (F) to 133.0 (H) with Δ_{CC} = 3.2 pm. For the unsaturated nitrogen rings, the changes are Δ_{CC} = 3.4 pm (130.2 (F) to 126.8 (H)), and

for the carbon rings they are Δ_{CC} = 2.6 pm (131.3 (F) to 128.7 (H)). The CC distances for the rings with X = N, C are even shorter than a double bond in acyclic systems, but these bond lengths are mostly dictated by the short CX bonds and the nitrogen or carbon hybridizations. This contrasts with the CC distances in the cyclopropenium cation (which is monosubstituted at X) of 136.3 pm [24] (135.9 pm, B3LYP/6-311+G(2d,p), this work). Since the CC single bonds are weaker, they can be elongated more easily and the changes Δ_{CC} are larger, with 11.9 (P), 8.1 (Si), 4.2 (N) and 4.4 (C) pm. These values are almost twice as large as for the double bonds for rings with third row elements, suggesting some hyperconjugative effect even in the saturated rings. In the **AS** with X = P, Si we find strongly elongated CC single bonds for Y = F, e.g. 164.3 pm for $(CH)_2PF_2^+$ and 163.4 pm for $(CH)_2SiF_2$, respectively.

The CX distances in the **AU** are shorter by about 3 to 5 pm than in the **AS**. The CX bonds for both types of phosphorus rings are shortened compared to the standard CP single bond, indicating some excess bonding interaction, with changes of Δ_{CX} = -7.2 pm for the **AU** and Δ_{CX} = -7.8 pm for the **AS**. For the silicon rings these changes are smaller (-5.1 and -5.5 pm) and the C-Si bond in the saturated ring with Y = H is 185.8 pm, identical to the literature value. The CN bonds range from 144 to 150 pm for the unsaturated (Δ = -9.3 pm) and from 146 to 150 pm for the saturated rings (Δ = -3.1 pm), the tabulated value (147 pm) intermediate, whereas the CX
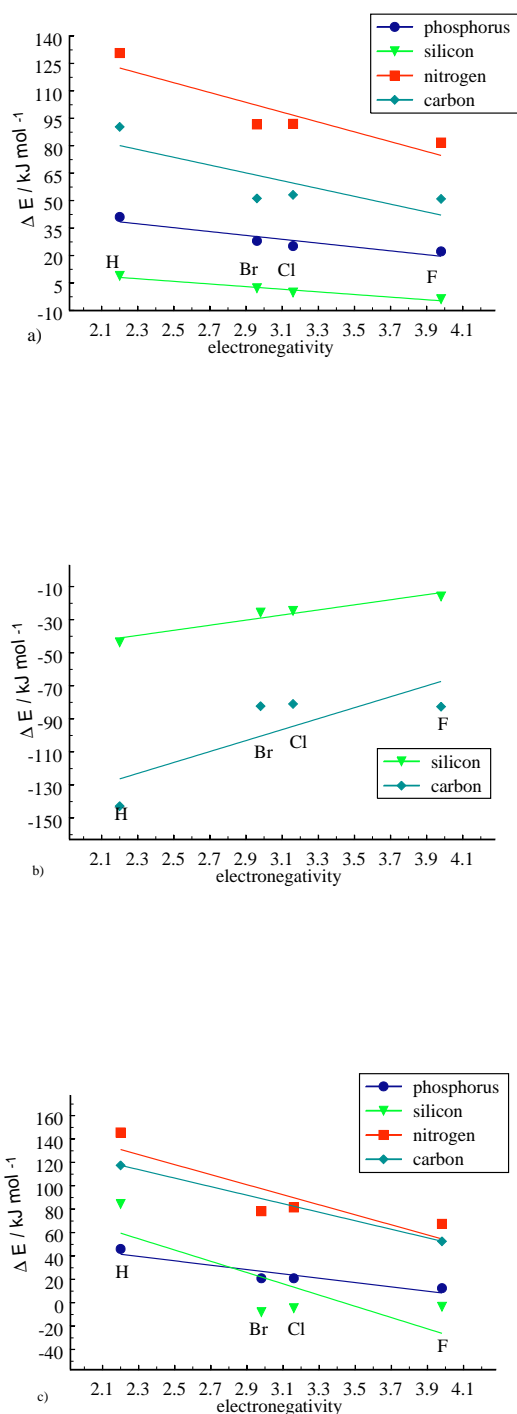
(X = C) bond distances in the carbon rings are always smaller than the CC single bonds of non-constrained molecules, but significantly longer than in the cyclopropenium cation. Here, the changes Δ are -6.6 for **AU** and -3.3 for **AS**.

When comparing the compounds with X from main groups IV and V, the changes are more pronounced for phosphorus and nitrogen than for silicon and carbon. Note that we formally compare positively charged P^+ or N^+ with neutral Si^0 or C^0. Thus, we have smaller atomic radii with steric constraints different from those of neutral cores [25], and also a lower electron density and a higher electron affinity at the group V elements, leading to shorter CX bonds.

The changes in the CXC and YXY angles are directly connected to the changes in the distances. The Δ_{CXC} are larger (see Table 1) for the **AS** than for the **AU** for X = P, Si and *vice versa* for X = N, C, and larger for the charged than for the uncharged rings. This finding is in close agreement with the results of Gordon [26], who showed that silacyclopropanes are more strained than cyclopropanes, whereas the reverse is true for the unsaturated silacyclopropenes and cyclopropenes. For the silacyclopropenes the Δ_{CXC} is only 2.45°, but with small angles for all rings, which has consequences for the ring strain energies discussed later. The angles are larger for the **AS** than for the **AU** and smaller for the second row than for the first row rings, with ~45° for the **AU** and ~51° for the **AS** (X = P, Si) and ~53° for the **AU** and ~60° for the **AS** (X = N, C), as a result of different hybridization tendencies.

The changes in YXY angles are unpredictable, but are smaller than those for the YX-lone-pair angles in the compounds of type **C**. They are generally somewhat larger for the **AS** than for the **AU**, and the Δ_{CXC} for the latter are larger. In Figures 2a to 2d, we present these findings as plots. The correlations of CX bond lengths *vs* electronegativity for the **AU** and the **AS** with X = P, Si are generally well-behaved, whereas the ones for the rings with X = N, C are not at all. The slopes are steeper for the latter. For the CC bond lengths, all correlations are reasonable, with positive slopes. The deviations are found mostly for bromine substituents, which are treated using using an bromine-optimized basis set rather than a standard one.

Even though the correlations are quite good at least for the second row elements, the geometric criterion can not be used as an indicator for σ^*-aromaticity. The changes Δ_{CC} in saturated rings are more pronounced than in the unsaturated ones, since the bonds are weaker and can therefore be elongated more easily. This flexibility causes changes in the strongly correlated CX bond lengths and also in the XY bonds and all angles. Thus, small changes in electron density cause large changes in the strongly coupled geometric parameters of the three-membered rings.

Ring strain energies Experimentally ring strain energies can be obtained from the comparison of the heats of combustion of two rings or from the energies of hydrogenation. Analogously one can define isodesmic reactions to compare the energies of unstrained compounds to the ones of strained rings. The reactions we use [9,27] (Scheme 4) give a measure of the extent of stabilization resulting from cyclic conjugation

Figure 3 *B3LYP/6-311+G(2d,p) calculated differences in ring strain between saturated rings and unsaturated rings* vs *electronegativity for (**a**) disubstituted* σ^**-aromatic **AU** over **AS**, (**b**) monosubstituted* π*-aromatic **BU** over **BS**, and (**c**) monosubstituted **CU** over **CS***

(aromaticity, antiaromaticity), hyperconjugation (σ*-aromaticity) as well as changes in hybridization at X, changes in steric repulsions of hydrogens and ligands Y, summed up to give strain energy.

If there is any σ*-aromatic stabilization, we expect to find a lowered strain energy in the **AU** compounds compared to, e.g., the strain energy difference in the pair cyclopropene/cyclopropane, which differ by about 88 kJ mol⁻¹.

The ring strain energies for the **AS** become smaller with less electronegative Y for all X, with larger values and changes for X = P, Si. The neutral **AS** (X = Si, C) release more strain energy than their charged counterparts (X = P, N). For the **AU** the picture is more complicated. For X = P we find no correlation, (-146 (F), -119 (Cl), -113 (Br), -176 kJ mol⁻¹(H)), for X = Si constant lowering, and for X = N, C a clustering in similar values for Y = F, Cl, Br and Y = H.

This results in systems with the largest energy difference between unsaturated and saturated rings being the ones with X = N, followed by the carbon, the phosphorus and the silicon rings (see Figure 3a and Table 2). Thus, the unsaturated rings with the second row elements profit from stabilization, whereas the first row elements almost do not. The strain energy differences ΔE become smaller for the more electronegative substituents, i.e., for larger hyperconjugative σ*-aromatic stabilization of the unsaturated rings. In detail, for phos-

Table 3 *B3LYP/6-311+G(2d,p) calculated σ*-aromatic stabilization energies*

Y	phosphorus	silicon	nitrogen	carbon
ΔE = AS - AU				
F	-18.89	-12.75	-48.95	-39.33
Cl	-15.93	-9.16	-38.77	-37.16
Br	-13.08	-6.81	-39.03	-39.08
ΔΔE [a]	-5.81	-5.94	-9.92	-0.25
ΔE = BS - BU				
F		+27.71		+60.19
Cl		+19.02		+61.78
Br		+17.97		+60.48
ΔΔE [a]		-9.74		+0.29
ΔE = CS - CU				
F	-33.48	-87.95	-78.12	-64.96
Cl	-25.16	-89.16	-64.08	
Br	-25.11	-92.46	-67.26	
ΔΔE [a]	-8.37	+4.51	-10.86	

[a] $\Delta\Delta E = \Delta E_{Y=H} - \Delta E_{Y=F}$.

Scheme 5 *Homodesmic reactions for determining the relative stabilities of unsaturated and saturated rings (σ*-aromatic stabilization energy). Reactions (**a**) are defined for the σ*-aromatic compounds of type **A**, reactions (**b**) for the π-aromatic **B** and reactions (**c**) for the non-aromatic **C***
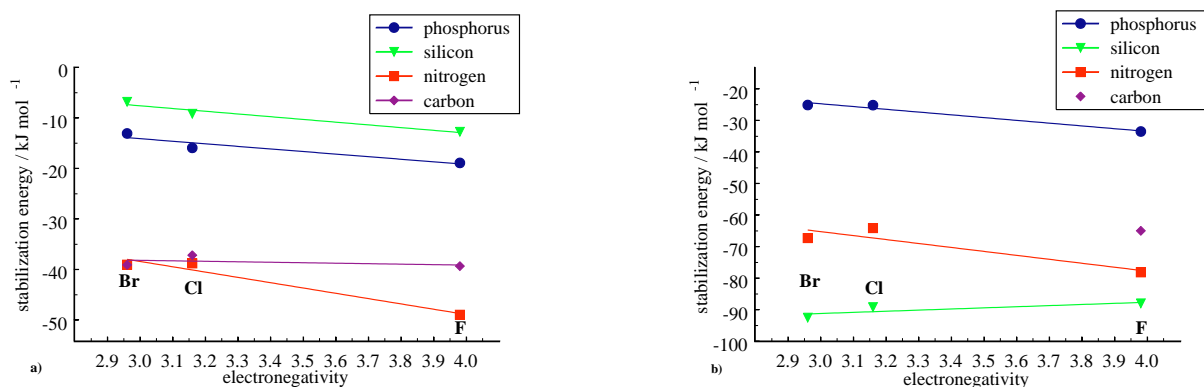

a)

X = P⁺, Si, N⁺, C

b)

X = Si⁺, C⁺

c)

X = P, Si̇, N, C⁻
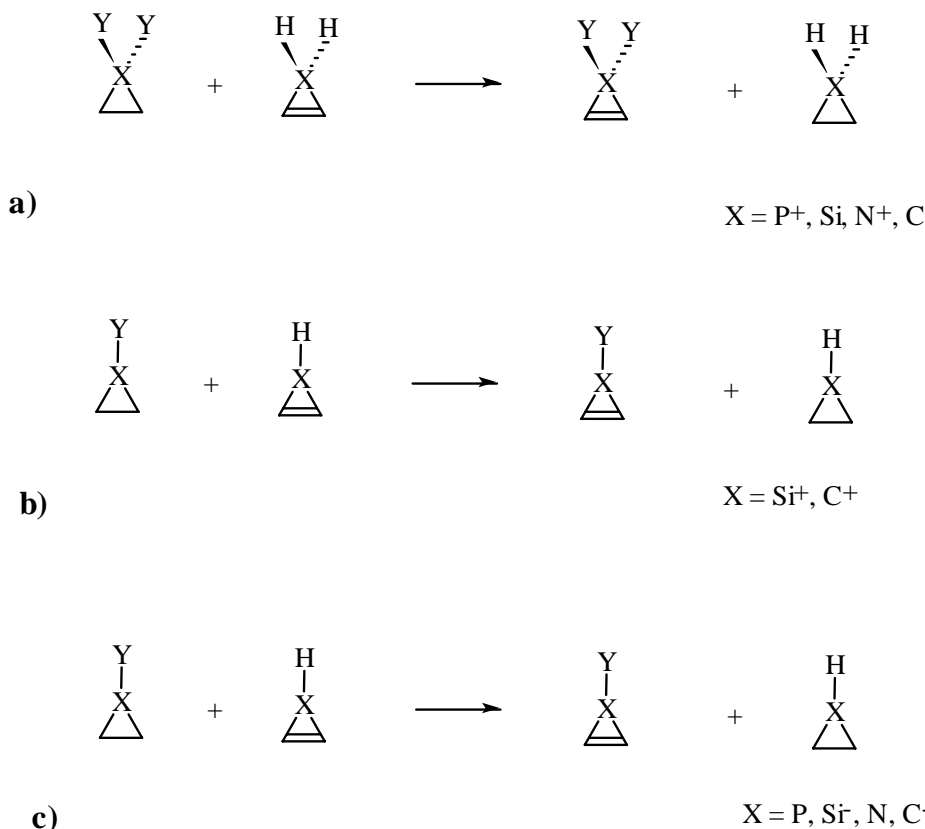
Figure 4 σ*-*aromatic stabilization energies of unsaturated over saturated rings* vs *electronegativity for (***a***) disubstituted AU over AS and (***b***) monosubstituted CU over CS*

phorus, the values are only 22.3 (F) and 41.2 (H) kJ mol^{-1}, whereas for nitrogen we find 81.8 (F) and 130.8 (H) kJ mol^{-1}. There is no visible correlation for X = N, C, but fairly good ones for X = P, Si. The $\Delta\Delta E$ for the former are quite large with 48.9 (N) and 39.3 (C), and smaller for the latter with 18.9 (P) and 12.7 (Si). The silicon rings show different behavior, in that there the ΔE are very small and even negative for Y = Cl (-0.2 kJ mol^{-1}) and Y = F (-3.8 kJ mol^{-1}). This can be explained by the unusually small CSiC angles in the silacyclopropenes discussed before [26]. Thus, the ΔE here are an admixture of σ*-aromatic effects (which should be larger for charged compounds [14]) and hybridization effects, which are more advantageous for the silicon rings. Therefore, the ring strain energies do not give a quantitative measure of σ*-aromaticity.

σ*-*aromatic stabilization*

The problems of the isodesmic reactions from the last paragraph can be overcome by the use of the homodesmic reactions [9,13] shown in Scheme 5. These eliminate (i) all the hybridization effects at the atoms X and (ii) all ring strain effects, by providing saturated and unsaturated rings and the same substitution pattern for reactants and products. These reactions give the stabilization directly by exchanging the ligand hydrogen at the unsaturated ring by a more electronegative substituent. Therefore, they provide a measure of the stabilization relative to that caused by the ligand hydrogen at X, assuming that hydrogen gives almost no σ*-aromatic stabilization.

As a result we obtain negative reaction energies for all rings (Figure 4a and Table 3), and even more negative ones for the first row elements, with silicon exhibiting almost no stabilization. The values are in the range of -18.9 to -13.1 kJ mol^{-1} for phosphorus, -12.8 to -6.8 for silicon, -49.0 to -39.0 for nitrogen and -39.3 to -39.1 kJ mol^{-1} for carbon.

There are weak, but significant changes in σ*-aromatic energies, correlated to ligand electronegativity, for the different substituted rings with X = P, Si, N, but none for the carbon rings. This is contrary to the results based only on the second-row elements phosphorus and silicon. The reason is that the overlap of the p-orbital at X and those forming the double bond is much better for the first row elements with
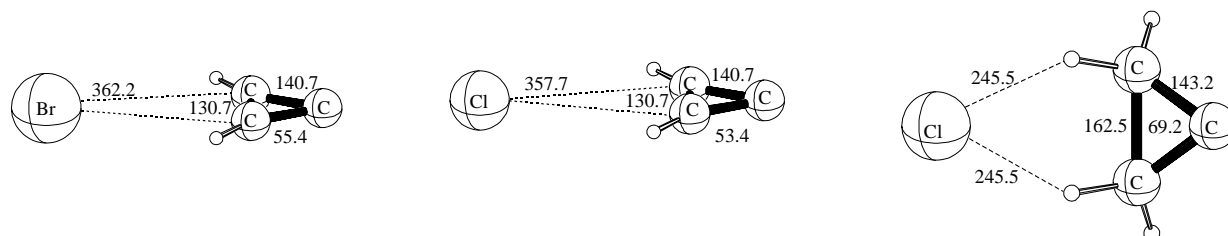
Scheme 6 *Structures **CU** with Y = Br, Cl and **CS** with Y = Cl have minima which are carbene-halogenide-complexes*

Table 4 *Bond lengths and angles for the structures of type* **BU** *and* **BS** *(see Scheme 3)*

Y	method	BU			BS		
		XC	CC	**CXC**	**XC**	CC	**CXC**
silicon							
F	HF [a]	170.8	138.8	47.93	177.5	166.1	55.80
	B3 [b]	173.4	141.4	48.14	177.1	169.9	57.33
Cl	HF	171.9	137.9	47.28	178.9	162.9	54.17
	B3	174.3	140.3	47.46	178.5	165.9	55.40
Br	HF	174.5	139.1	46.96	180.3	163.1	55.77
	B3	174.5	140.0	47.20	179.1	164.6	54.70
H	HF	172.7	137.1	45.79	180.4	159.0	52.28
	B3	175.0	139.0	46.81	180.0	160.8	53.12
Δ [c]	HF	-1.9	1.7	0.08	-2.9	7.1	3.52
	B3	-1.6	2.4	1.33	-2.9	9.1	4.21
carbon							
F	HF	134.3	136.2	59.54	140.3	156.7	66.95
	B3	135.7	137.4	60.81	140.7	160.3	69.41
Cl	HF	135.2	135.0	59.88	143.9	153.1	64.32
	B3	136.9	135.7	59.44	142.7	156.1	66.28
Br	HF	137.7	136.5	54.45	146.0	152.7	63.06
	B3	137.0	135.4	59.22	143.0	155.5	65.67
H	HF	134.9	135.0	60.04	143.8	151.1	63.36
	B3	135.9	135.9	60.00	141.8	153.6	65.81
Δ	HF	-0.6	1.2	-0.50	-3.5	5.6	3.59
	B3	-0.2	1.5	0.81	-1.1	6.7	3.60

[a] HF = HF/6-31G(d)
[b] B3 = B3LYP/6-311+G(2d,p)

[c] Δ is the difference between the value for Y = F and Y = H

contracted orbitals than for the second row elements with more diffuse ones.

π-aromatic compounds

Structures The π-aromaticity [5] and inherent chemical lability [6,8] of phosphirenylium cations have been discussed previously. The nitrogen rings are similar.

The XC bond lengths of the **BU** structures (see Table 4) are shortened relative to those in **AU** on going from Y = F to Y = H by 3 to 7 pm for X = Si and by a constant 9 pm for X = C, and for the **BS** *vs* the **AS** these bonds are shortened by 3 to 6 pm for X = Si, but 6 to 9 pm for X = C (compared to Table 1). At the same time the CC distances are elongated by about the same amounts as the CX are shortened.

The Δ_{CX} and Δ_{CC} going from Y = F to H are very small for the **BU**, since the p-orbital participating in the aromatic 3c-2e-interaction is perpendicular to the electronegative substituent, in contrast to the σ*-orbital responsible for the 3c-2e-interaction in the σ*-aromatic **AU**. In the **BS**, the σ-type CC single bond can be polarized by the σ-type XY-bond, by electronegative ligands Y. This is not the case in the **AS**.

The result is a much more pronounced bond elongation for CC in the **BS**, but a CX bond shortening similar to the **AS**.

As a result of the different CC and CX distances, all CXC angles are larger by about 3-4° for X = Si and 5-10° for X = C. The correlations of bond lengths *vs* electronegativity are generally good for the silicon rings and poor for the carbon rings, as shown in Figure 5. We find two pairs, the soft and polarizable chlorine and bromine and the hard fluorine and hydrogen [28].

Ring strain energies Because of their π-aromatic character, the silacyclopropenes and the cyclopropenes are less strained than their saturated counterparts. Thus, from our definition of the ring strain energy difference ΔE as the difference in exothermicity of the saturated and unsaturated ring openings for the reactions in Scheme 4b, the numbers here must become negative (Table 2). They are more negative for the carbon rings, ranging from -15.9 to -43.6 for silicon and from -82.6 to -142.7 kJ mol^{-1} for carbon rings going from Y = H to Y = F. Thus, electronegative Y destabilizes the aromatic ring.

Therefore, as expected, we find a dependency contrary to the one for the σ*-aromatic compounds because of strong π-aromatic stabilization of the unsaturated rings. As for the bond
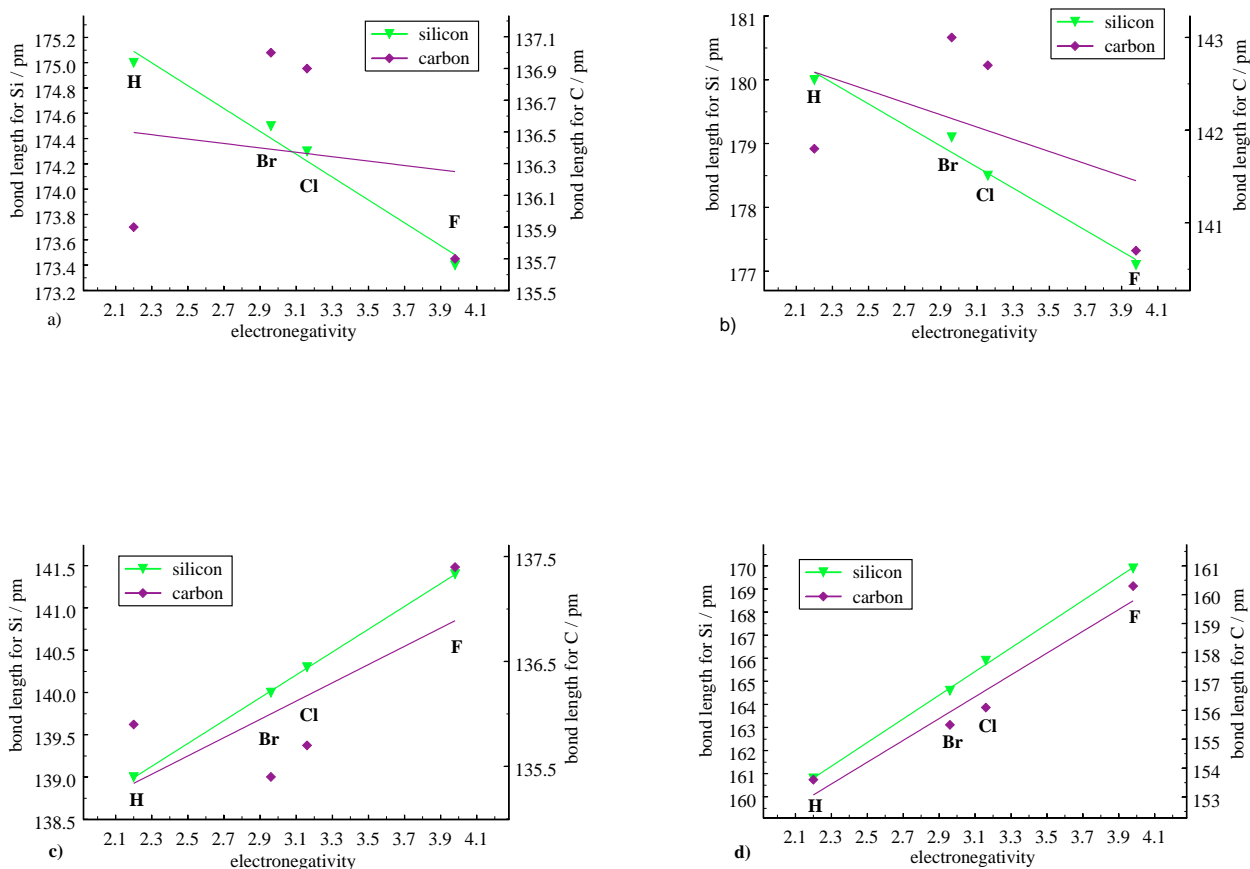
Figure 5 *Changes in bond lengths Δ_{CX} (**a**, **b**) and Δ_{CC} (**c**, **d**) for unsaturated (**a**, **c**) and saturated (**b**, **d**) π-aromatic rings **BS** and **BU**(X = Si, C), B3LYP / 6-311+G(2d,p) optimized*

length alterations, there is a good correlation (Figure 3b) for X = Si and clustering in pairs for X = C.

Destabilization of the π-aromatic system instead of σ- aromatic stabilization*

The π-aromatic stabilization of the **BU** rings is the dominant contribution, which causes the homodesmic reactions in Scheme 5b to become endothermic, i.e., destabilization of the unsaturated compared to the saturated halogen-substituted rings. The reaction energies are correlated to substituent electronegativity (Table 3) for silicon, but not for carbon rings.

σ-Non-aromatic compounds*

The last compound classes we discuss are the monosubstituted 1*H*-phosphirenes (**CU**) and 1*H*-phosphiranes (**CS**) and their isoelectronic analogs. The systems are neutral for X =

P, N and negative for X = Si, C, with a lone-pair at X, which is involved in an unfavorable 3c-4e interaction with the CC bond. This raises the energies of all unoccupied orbitals. Thus, the σ*-orbital from the XY moiety is (i) high-lying, and (ii) does not have the appropriate symmetry. Therefore, the geometries and energetics should not be correlated to ligand electronegativity.

Structures 1*H*-phosphirenes are available with a large variety of substitution patterns [3,29]. The 1*H*-Azirines, on the other hand, have only been found as very unstable intermediates [30]. The cyclopropenium anions are intermediates for proton exchange. We have been unable to find any investigations at all on the silacyclopropenium anions.

All have the same structural characteristics. The substituent Y is out-of-plane and the compounds are C_s symmetric. There are three deviations, namely (CH)$_2$CCl, (CH)$_2$CBr and (CH$_2$)$_2$CCl, shown in Scheme 6. These are weak singlet carbene-halogenide complexes [31]. The unsaturated (CH)$_2$CCl and (CH)$_2$CBr are C_{2v}, the latter is C_s symmetric.

Table 5a *Bond lengths and angles for the structures of type **CU** and **CS** (see Scheme 3)*

| Y | method | CU | | | | CS | | | |
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
phosphorus									
F	HF [a]	177.3	130.0	43.02	106.27	182.6	150.6	47.84	101.34
	B3 [b]	180.0	130.7	42.59	105.27	185.2	150.2	48.70	100.89
Cl	HF	177.9	129.6	42.71	106.66	184.0	149.7	48.00	102.38
	B3	180.5	130.4	42.36	106.31	186.2	149.7	47.38	102.04
Br	HF	187.3	130.1	40.64	105.05	191.7	148.6	45.61	100.98
	B3	180.5	130.4	42.34	106.52	186.7	149.4	47.17	102.21
H	HF	182.1	128.3	41.25	102.42	185.3	149.2	47.49	97.81
	B3	185.2	129.0	40.77	100.36	187.7	149.2	46.83	96.05
Δ [c]	HF	-4.8	1.7	1.77	3.85	-2.7	1.4	0.35	3.53
	B3	-5.2	1.7	1.82	4.91	-2.5	1.0	1.87	4.84

[a]HF = HF/6-31G(d)
[b] B3 = B3LYP/6-311+G(2d,p)

[c] Δ is the difference between the value for Y = F and Y = H

Table 5b *Bond lengths and angles for the structures of type **CU** and **CS** (see Scheme 3)*

| Y | method | CU | | | | CS | | | |
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
silicon									
F	HF [a]	188.7	132.0	40.94	105.31	192.7	153.7	46.99	100.61
	B3 [b]	190.8	132.6	40.68	104.57	194.6	153.0	46.29	100.44
Cl	HF	186.0	131.9	41.51	103.34	192.2	152.7	46.82	98.75
	B3	189.0	132.4	41.01	103.44	194.4	152.2	46.09	98.74
Br	HF	183.3	133.7	41.57	103.08	193.9	153.5	46.65	98.39
	B3	188.3	132.5	41.20	103.54	194.2	152.1	46.11	98.61
H	HF	191.2	130.8	39.99	102.42	194.3	152.5	46.19	97.18
	B3	193.9	131.5	39.65	101.08	196.6	151.8	45.42	96.31
Δ [c]	HF	-2.5	1.2	0.95	2.89	-1.6	1.2	0.80	3.43
	B3	-3.1	1.1	1.03	3.49	-2.0	1.2	0.87	4.13

[a]HF = HF/6-31G(d)
[b] B3 = B3LYP/6-311+G(2d,p)

[c] Δ is the difference between the value for Y = F and Y = H

The carbene-like structure has the advantage of an empty p-orbital at X that interacts with the double bond similar to π-aromatic-like rings.

For the regular structures we find CX distances in the range of the tabulated bond lengths for non-constrained systems, without any correlation to ligand electronegativity. For the **CU**, there is some clustering, i.e., similar values for Y = F, Cl, Br and a different one for Y = H (e.g. X = P: 180.0, 180.5, 180.5 and 185.2 pm). For the **CS**, there is a weak but not significant change for X = P, Si (Δ_P= -2.5 pm; Δ_{Si} = -2.0 pm) and no change at all for X = N, C.

The CC bonds are even less influenced by the ligand. Here, the values stay constant and are only dictated by strain in the ring skeleton.

The lone-pair at hetero atom X occupies more space than a ligand atom, so the angles of the XY bond with the ring plane are more out-of-plane than for the disubstituted species. The unsaturated phosphorus rings **CU** have angles of about 106° for Y = F, Cl, Br and 100° for Y = H, compared to values of about 124-129° (180° minus half the YXY angle listed in Table 1).

Ring strain energies The ring strain energies of compounds **CU** and **CS** (Table 2) as defined in Scheme 4c are also clustered in smaller negative numbers for rings with Y = F, Cl, Br and large negative ones for Y = H, as shown in Figure 3c. This contrasts with the **AU** and **AS** rings of the first section, where the exothermicity decreases with less electronegative

Table 5c *Bond lengths and angles for the structures of type* **CU** *and* **CS** *(see Scheme 3)*

Y	method	CU				CS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
nitrogen									
F	HF [a]	143.3	126.3	52.29	108.71	144.9	147.1	60.99	110.72
	B3 [b]	143.3	128.4	53.23	106.80	147.4	148.2	60.37	109.80
Cl	HF	142.2	126.7	52.89	113.00	145.1	147.3	61.00	118.79
	B3	143.6	128.5	53.16	111.69	147.6	148.3	60.30	116.15
Br	HF	148.5	128.2	51.13	116.72	147.0	149.2	60.99	124.20
	B3	143.2	128.7	53.43	112.80	147.4	148.4	60.45	117.72
H	HF	149.0	125.5	49.81	110.79	144.9	147.1	61.04	115.45
	B3	152.1	126.9	49.32	109.29	147.3	148.2	60.41	113.63
Δ [c]	HF	-5.7	0.8	2.48	-2.08	0.0	0.0	-0.05	-4.73
	B3	-8.8	1.5	3.91	-2.49	0.1	0.0	-0.04	-3.83

[a] HF = HF/6-31G(d)   [c] Δ is the difference between the value for Y = F and Y = H
[b] B3 = B3LYP/6-311+G(2d,p)

Table 5d *Bond lengths and angles for the structures of type* **CU** *and* **CS** *(see Scheme 3)*

Y	method	CU				CS			
		XC	CC	CXC	YXY	XC	CC	CXC	YXY
carbon									
F	HF [a]	151.4	128.4	50.17	105.10	152.6	150.2	58.98	106.50
	B3 [b]	149.4	130.0	51.58	103.00	152.7	151.4	59.45	107.94
Cl	HF								
	B3								
Br	HF					153.5	150.6	58.74	103.77
	B3					153.0	150.6	58.97	108.76
H	HF	158.1	128.0	47.74	106.90	152.5	150.4	59.11	110.58
	B3	157.0	129.4	48.69	109.77	152.7	151.3	59.41	113.22
Δ [c]	HF	-6.7	0.4	2.43	-1.80	0.1	-0.2	-0.13	-4.08
	B3	-7.6	0.6	2.89	-6.77	0.0	0.1	0.04	-5.28

[a] HF = HF/6-31G(d)   [c] Δ is the difference between the value for Y = F and Y = H
[b] B3 = B3LYP/6-311+G(2d,p)

ligand. The energy differences ΔE are positive - the ring strain in unsaturated **CU** is higher than in **CS** - and also clustered.

The ring opening reactions are always less exothermic by more than 50 kJ mol^{-1} than for the disubstituted **AU** and **AS**. The ΔE, on the other hand, are in the same range for both compound classes, but not correlated to ligand electronegativity for the monosubstituted structures.

σ*-Aromatic stabilization in monosubstituted rings?

The stabilization of the unsaturated compared to the saturated rings given by the homodesmic ligand exchange reactions in Scheme 5c are always more exothermic than for the reactions of compounds **AS** and **AU**, Scheme 5a. There is no obvious correlation to ligand electronegativity (reaction energies are given in Table 3). For the neutral rings, the reactions with fluorine ligands are more exothermic by 8 kJ mol^{-1} (X = P) and 11 kJ mol^{-1}(X = N) than for Y = Br, Cl; for silicon the ranking is reverse. (For carbon there is only one value for Y = F.) This is because of the destabilization due to the high electron density in the ring caused by the lone-pair. This is in contrast to the σ*-aromatic 1*H*-phosphirenium cations and their analogs, where the XY$_2$ moiety σ*-MO is lowered due to ligand electronegativity. The electron density in the ring in the **CS** is even raised by the positive inductive effect of four hydrogens interacting with the appropriate p-orbitals at the carbon ring atoms, contrary to the **CU**, where the carbon-hydrogen bonds have a nodal plane with the p-orbitals at the ring sceleton atoms.

Summary

In phosphorus chemistry, we find three types of unsaturated three-membered rings, the phosphorenylium cations **1** unsubstituted at phosphorus, the monosubstituted 1*H*-phosphirenes **2**, and the disubstituted 1*H*-phosphirenium cations **3**. These have different bonding situations and also differently shaped molecular orbitals and electron distributions, which in turn give rise to interesting structural and energetic features depending on the substitution patterns.

Cation **1** is a π-aromatic system like the cyclopropenium cation. The ions **3** show a significant weak hyperconjugative σ*-aromatic stabilization, which results from the interaction of the low-lying σ*-orbital of the PY_2 fragment with the HC=CH fragment. This stabilization is larger for more electronegative ligands Y. In the 1*H*-phosphirenes **2**, the out-of-plane lone-pair at phosphorus does not permit this kind of bonding interaction. Instead it occupies much more space than normal substituents, as can be seen from the bond angles, and raises the orbital energies of the virtual MO's. Therefore, there is no substituent effect in the 1*H*-phosphirenes **2**.

The geometrical consequences are ligand electronegativity correlated elongations of CC bond lengths and shortenings of the CP distances, relative to the tabulated values for non-constrained systems, for 1*H*-phosphirenium cations **3**, but also for their saturated analogs, the 1*H*-phosphiranium cations **4**. There is no such effect for the 1*H*-phosphirenes **2,** which experience no σ*-aromatic stabilization, and also not for their saturated counterparts, the 1*H*-phosphiranes. For the π-aromatic silacyclopropenes and cyclopropenes, as for their saturated analogs, the elongations of CC and shortenings of CX bonds are even more pronounced, since π-aromaticity is a stronger effect than hyperconjugation.

If we exchange phosphorus by silicon, nitrogen, or carbon, the same geometrical changes with substitution pattern occur on rings of types **A** and **C**, as discussed for the phosphorus heterocycles. For the second row elements phosphorus and silicon, the bond lengths are correlated to ligand electronegativity. In the nitrogen and carbon rings, effects like steric repulsion are more important because of the small ring size, and there is no obvious correlation. The different hybridization tendencies also play an important role, as can be seen from the much larger first row element CXC ring angles.

All ring opening reactions shown here are exothermic, since they release strain. For compounds of types **A** and **C**, the unsaturated rings are more strained than the saturated ones, for the π-aromatic **B**, they are less. Thus, the use of more electronegative ligands is favorable for the disubstituted **A** and unfavorable for the monosubstituted π-aromatic **B**. The monosubstituted **C** are uninfluenced.

The same picture is obtained from homodesmic substituent exchange reactions, which are the best available measure for the σ*-aromatic effect. The structures **A** profit from more electronegative ligands, the **C** are unaffected and the **B** are destabilized, so their reactions become endothermic.

Conclusions

σ*-aromaticity is a weak hyperconjugative effect. It stabilizes the electronegative disubstituted 1*H*-phosphirenium cations **3** over saturated 1*H*-phosphiranium cations **4**. But since this effect is so weak, it is often covered by steric effects and ring strain. These unfavorable effects force the ring atoms to deviate from optimum bonding interactions with neighbors and cause energetic penalties larger than σ*-aromatic benefits. The destabilization by electronegative substituents in π-aromatic systems is a rather strong and obvious effect. The complete absence of energy or geometry correlations to ligand electronegativity in the monosubstituted rings of type **C**, on the other hand, is an indirect proof of the existence of σ*-aromaticity. To obtain a picture of σ*-aromaticity less influenced by side effects, less constrained rings must be studied.

References

1. (a) Breslow, R. J.; Groves, J. T.; Ryan, G. J. *J. Am. Chem. Soc.* **1957**, *79*, 5318. (b) Ciabattoni, J.; Nathan III, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 4766. (c) Sunderlingham, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.
2. Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10.
3. (a) Regitz, M. *Chem. Rev.* **1990**, *90*, 191. (b) Regitz, M.; Binger, P. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; pp 58-111. (c) Regitz, M. *J. Heterocycl. Chem.* **1994**, *31*, 663. (d) Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225. (e) Wagner, O.; Ehle, M.; Hoffmann, J. *Chem. Ber.* **1991**, *124*, 1207.
4. (a) Fongers, K. S.; Hogeveen, H.; Kingma, R. F. *Tetrahedron Lett.* **1986**, *24*, 643. (b) Lochschmidt, S.; Mathey, F. *Tetrahedron Lett.* **1986**, *27*, 2635. (c) Breslow, R.; Deuring, L. A. *Tetrahedron Lett.* **1984**, *25*, 1345. (d) Vural, J. M.; Weissmann, S. A.; Baxter, S. G.; Cowley, A. H.; Nunn, C. M. *J. Chem. Soc., Chem. Commun.* **1988**, 462. (e) Weissmann, S. A.; Baxter, S. G. *Tetrahedron Lett.* **1990**, *31*, 819.
5. (a) Maclagan, G. A. R. *Chem. Phys. Lett.* **1989**, *163*, 349. (b) Largo, A.; Barrientos, C.; Lopez, X.; Cossio, F.; Ugalde, J. M. *J. Phys. Chem.* **1995**, *99*, 6432.
6. Laali, K. K.; Geissler, B.; Wagner, O.; Hoffmann, J.; Armbrust, R.; Eisfeld, W.; Regitz, M. *J. Am. Chem. Soc.* **1994**, *116*, 9407.
7. Memmesheimer, H.; Regitz, M. *Rev. Heteroat. Chem.* **1994**, *10*, 61.
8. Eisfeld, W.; Regitz, M. *J. Org. Chem.* **1998**, *63*, 2814.

9. (a) Göller, A.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840. (b) Göller, A. *Problemangepaßte quantenchemische Berechnungen zu Cytochrom P450-Metabolismus und σ*-Aromatizität*, Thesis, Friedrich-Alexander-Universität Erlangen-Nürnberg: Erlangen, 1997; pp. 67-143.

10. Hockless, D. C. R.; McDonald, M. A.; Pabel, M.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1995**, 257.

11. (a) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027. (b) Koppel, I. A.; Phil, V.; Koppel, J.; Anvia, F.; Taft, R. W. *J. Am. Chem. Soc.* **1994**, *116*, 8654, and references therein.

12. (a) Greenberg, A.; Liebman, J.; Dolbier, W.R., Jr.; Medinger, K. S.; Shancke, A. *Tetrahedron* **1983**, *39*, 1533. (b) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689.

13. Borden, W. T. *J. Chem. Soc., Chem. Commun.* **1998**, 1919.

14. Kutzelnigg, W. *Einführung in die theoretische Chemie*; VCH: Weinheim, 1978; Vol. 2, p 328.

15. Pauling, L. *The Nature of the Chemical Bond*, 3rd. ed.; Cornell Univ. Press: Ithaca, New York, 1960.

16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, J. R.; Cheeseman, T.; Keith, G. A.; Peterson, 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, A.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J.A. Gaussian, Inc., Pittsburgh PA, 1995.

17. (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

18. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

19. (a) Krishnan, R.; Pople, J.A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

20. (a) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, 1993; b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford Science Publications: New York, 1989.

21. Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

22. Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Brinkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *J. Quantum Symp.* **1981**, *15*, 269.

23. (a) Aylward, G. H.; Findlay, T. J. V. *Datensammlung Chemie*, 2nd ed., VCH: Weinheim, **1986**.(b) MP2/6-31+G*//MP2/6-31+G* calculated bondlength for $H_2Si=CH_2$.

24. Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

25. Catalán, J.; Yáñez, M. *J. Am. Chem. Soc.* **1978**, *100*, 1938.

26. Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 163.

27. (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986. (b) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

28. (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581.

29. Heydt, H; Ehle, M; Haber, S.; Hoffmann, J.; Wagner, O.; Göller, A.; Clark, T.; Regitz, M. *Chem. Ber.* **1997**, *130*, 711.

30. Regitz, M.; Arnold, B.; Danion, D.; Schubert, H.; Fusser, G. *Bull. Soc. Chim. Belg.* **1981**, *90*, 615.

31. Moss, R. A. In *Carbenes*; Jones, M., Jr.; Moss, M. A., Eds.; Wiley & Sons: New York, 1973.