

σ^* -Aromaticity of Substituted 1*H*-Phosphirenium Cations and Substituted Silacyclopropenes[†]

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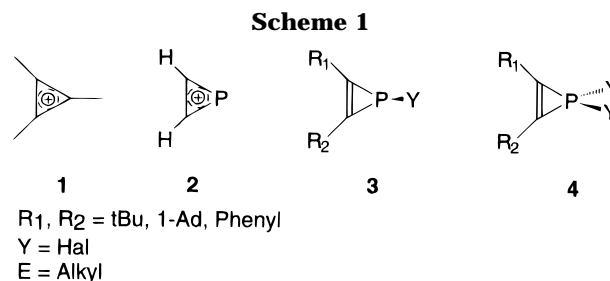
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The influence of the electronegativity of the ligands Y (F, Cl, Br, I, OH, NH₂, CH₃, H) on the strength of the σ^* -aromatic effect in gem-disubstituted 1*H*-Phosphirenium cations and substituted 3-silacyclopropenes has been investigated with *ab initio* theory. Phosphorus and silicon provide a low lying p-type σ^* -orbital antibonding to the ligands Y. This interacts with the ring double bond analogously to a third p-orbital in a 2*π* Hückel system. These systems have been compared to the analogous saturated rings. Calculations at the RHF/6-31G* and MP4/6-31+G* levels, NBO analyses of the effect of the ligands Y and comparisons of the relative stabilities of the saturated and unsaturated compounds suggest a weak but significant σ^* -aromatic effect dependent on the electronegativity of Y.

1. Introduction

An unsolved problem in the chemistry of phosphirene derivatives is the aromatic or antiaromatic character of cationic species derived by dissociation of a substituent at phosphorus to give the phosphorenylium cations **2** or by association of one electrophile to give phosphirenium cations **4**.¹ First synthesized by Breslow in the late 1950s,² the cyclopropenylium cation **1** has occupied a central position in experimental³ and theoretical⁴ carbocation chemistry as the smallest 2*π* Hückel aromatic compound. There is far less information about the phosphirenylium cation **2**, the phosphorus analog of cyclopropenylium ions. It is the lowest energy isomer on the C₂H₂P⁺-energy surface.⁵ Its C-substituted isomers have been discussed as intermediates in nucleophilic substitution reactions of 1*H*-phosphirenes, **3**, with a leaving group Y at the phosphorus atom.⁶ The first successful generation of a derivative of **2** in solution was achieved by ionization of **3** (R₁ = tBu, R₂ = Ph, Y = OTf) in SO₂/B(OTf)₃ at dry ice/acetone temperature under argon.⁷

The 1*H*-phosphirenium cations (**4**: Y = Cl, E = Me, Ph) can be formed by cycloaddition of phosphorus dichlorides and alkynes.⁸ Phosphinous chloride–aluminum trichloride complexes react analogously to give P,P-dialkylated and -diarylated structures (**4**: Y = E = Me,



Ph).⁹ Amino-substituent stabilized phosphirenium ions are also able to undergo [2 + 1] cycloadditions with alkynes to form the phosphirenium cation (**4**: Y = N(*i*-Pr)₂, E = alkenyl), whose structure has been confirmed by an X-ray crystal analysis.¹⁰

Another route to compounds **4** is the reaction of stable phosphiranium triflates with alkynes (**4**: Y, E = Me, Ph).¹¹ A wide range of stable phosphirenium cations can be obtained by reactions of 1*H*-phosphirene with alkylating reactants (**3** + E⁺ → **4**, see Scheme 2). Alkoxonium tetrafluoroborates¹² or -triflates¹³ play an outstanding role in this context.

The 1*H*-phosphirenes themselves are derived by [2 + 1] cycloaddition of alkyl or arylhalogenide carbenes (from thermolysis of diazirines **6**) and kinetically stabilized phosphalkynes **5**.¹⁴ The intermediate 2*H*-phosphirene **7** undergoes a fast 1,3-halogen shift to the more stable 1*H*-phosphirene **3**.¹⁵

1*H*-Phosphirenium cations **4** are also of considerable theoretical interest. A phosphorus orbital bisects the p-orbitals of the carbon–carbon bond of **4**, permitting a

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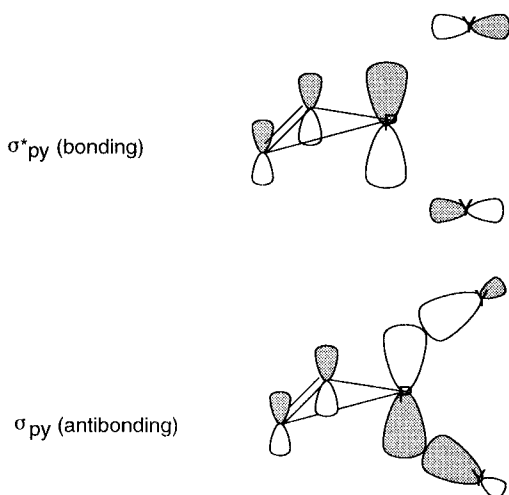
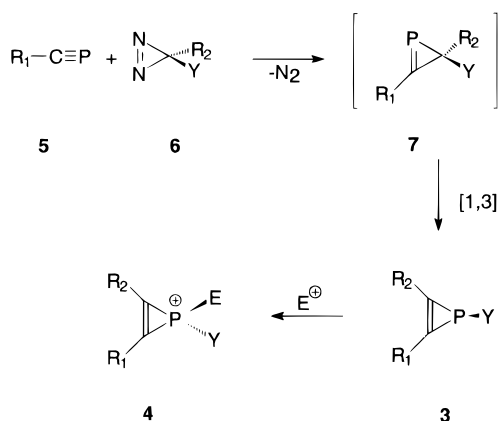


Figure 1. MO scheme for 1*H*-phosphirenium cations. The double-bond phosphorus interactions are stabilizing for the σ^*_{py} orbital and are destabilizing for the σ_{py} orbital.

Scheme 2. Synthesis of 1*H*-Phosphirenium Cation



R₁ = *t*-Bu, CMe₂Et, 1-Ad
R₂ = Phenyl, *t*-Bu, OR'
Y = F, Cl, Br

Hückel-type three-orbital two-electron interaction characteristic of cyclopropenyl cations. This p-type σ^* -orbital is phosphorus-ligand antibonding, so it is convenient to designate this interaction as σ^* -aromaticity.¹⁶ A large phosphorus coefficient in this p-type σ^* -orbital should increase the stabilizing aromatic interaction. This should be the case if electronegative substituents are bonded to phosphorus. However, **4** has an occupied p-type σ -orbital on phosphorus that can lead to some antiaromatic character. Therefore, electron-donating substituents at phosphorus should destabilize the system by strengthening antiaromatic interactions.

As a consequence, increased CC-bond lengths and decreased CP-bond lengths of the three-membered ring are expected in 1*H*-phosphirenium cations with electronegative ligands Y. In this contribution we focus our interest on σ^* -aromaticity and its consequences for the relative stabilities and geometrical changes of 1*H*-phosphirenium cations with hydrogens at the carbon atoms and different ligands (F, Cl, Br, I, OH, NH₂, CH₃, H) on

phosphorus. The isoelectronic substituted 3-silacyclopropenes have also been studied.

The electronegativity of the ligands should also influence the C=C hydrogenation energies and to some extent the relative stabilities of the analogous saturated phosphorus and silicon three-membered rings. For interpretative purposes we have chosen to use the Pauling¹⁷ electronegativity scale, although other approaches^{18–20} would also be appropriate, e.g. specialized scales for molecular fragments.²¹

There is also evidence from the experimental viewpoint for the existence of σ^* -aromatic stabilization. Wild et al.²² recently described the reaction of 1-phenyl-1-methylphosphirane with dimethylacetylene to form the corresponding phosphirenium salt in high yield.

Another class of compounds profits from the same stabilizing effects. Carpino et al.²³ discuss the synthesis and behavior of 2,3-diphenylthiirane 1,1-dioxide and 2,3-diphenylthiirene 1,1-dioxide and the enhanced thermal stability of the thiirene dioxides relative to the saturated compounds caused by conjugative effects.

2. Computational Methods

All structures except those containing bromine and iodine were first optimized using RHF/6-31G*²⁴ using Gaussian94.²⁵ These structures were refined using second order Møller–Plesset perturbation theory with the diffuse-augmented 6-31+G* basis set (MP2/6-31+G*).²⁶ MP2 optimizations used the frozen core approximation. The final energies were obtained with Møller–Plesset fourth order perturbation theory (MP4SDTQ/6-31+G*//MP2/6-31+G*).²⁷ For bromine a split valence basis set due to Schäfer, Horn, and Ahlrichs²⁸ was used, which was later extended with diffuse functions.²⁹ The iodine compounds were computed analogously but using effective core potentials.³⁰ The zero point vibrational energies were calculated at the RHF/6-31G* level (calibration factor 0.89³¹) on the RHF-optimized geometries.

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Table 1. Data for Molecular Geometries for Saturated Systems (lengths in Å, angles in deg) (HF = RHF/6-31G(d); MP2 = RMP2-FC/6-31+G(d))

		F	OH	Cl	NH ₂	Br	I	CH ₃	H
		(CH ₂) ₂ PY ₂ ⁺							
HF	<i>d</i> (C–P)	1.725	1.741	1.768	1.770	1.795	1.802	1.788	1.803
MP2		1.733	1.749	1.770	1.782	1.784	1.803	1.795	1.805
HF	<i>d</i> (C–C)	1.618	1.594	1.562	1.551	1.545	1.529	1.535	1.516
MP2		1.631	1.602	1.573	1.551	1.560	1.542	1.538	1.521
HF	<i>d</i> (P–Y)	1.512	1.555	1.958	1.632	2.147	2.384	1.810	1.377
MP2		1.550	1.587	1.962	1.649	2.139	2.383	1.803	1.392
	symmetry	C _{2v}	C ₂	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}
		(CH ₂) ₂ SiY ₂							
HF	<i>d</i> (C–Si)	1.801	1.813	1.817	1.832	1.835	1.834	1.847	1.851
MP2		1.811	1.821	1.826	1.840	1.833	1.844	1.857	1.862
HF	<i>d</i> (C–C)	1.621	1.609	1.593	1.595	1.582	1.572	1.569	1.555
MP2		1.624	1.611	1.595	1.596	1.586	1.575	1.565	1.549
HF	<i>d</i> (Si–Y)	1.578	1.638	2.042	1.709	2.222	2.449	1.882	1.469
MP2		1.616	1.669	2.038	1.723	2.211	2.450	1.877	1.477
	symmetry	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C _{2v}	C _{2v}	C _{2v}

Table 2. Data for Molecular Geometries for Unsaturated Systems (lengths in Å, angles in deg) (HF = RHF/6-31G(d); MP2 = RMP2-FC/6-31+G(d))

		F	OH	Cl	NH ₂	Br	I	CH ₃	H
		(CH) ₂ PY ₂ ⁺							
HF	<i>d</i> (C–P)	1.688	1.683	1.705	1.702	1.727	1.732	1.737	1.739
MP2		1.690	1.703	1.723	1.724	1.735	1.752	1.757	1.760
HF	<i>d</i> (C–C)	1.380	1.346	1.328	1.337	1.329	1.313	1.314	1.305
MP2		1.381	1.376	1.356	1.364	1.352	1.342	1.335	1.327
HF	<i>d</i> (P–Y)	1.545	1.557	1.961	1.602	2.151	2.392	1.810	1.378
MP2		1.550	1.590	1.966	1.636	2.145	2.393	1.804	1.395
	symmetry	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}	C _{2v}
		(CH) ₂ SiY ₂							
HF	<i>d</i> (C–Si)	1.754	1.770	1.767	1.786	1.784	1.779	1.804	1.802
MP2		1.772	1.786	1.785	1.802	1.790	1.800	1.822	1.822
HF	<i>d</i> (C–C)	1.352	1.351	1.343	1.346	1.345	1.336	1.331	1.326
MP2		1.380	1.379	1.368	1.373	1.366	1.367	1.354	1.347
HF	<i>d</i> (Si–Y)	1.578	1.635	2.045	1.709	2.228	2.457	1.885	1.473
MP2		1.615	1.665	2.041	1.724	2.216	2.457	1.880	1.481
	symmetry	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C _{2v}	C _{2v}	C _{2v}

3. Results

3.1. Geometries. Pauling's electronegativity scale gives the following sequence for the ligands Y (for polyatomic ligands the central atom is chosen):

F	3.98;	OH	3.44;	Cl	3.16;	NH ₂	3.04;
Br	2.96;	I	2.66;	CH ₃	2.55;	H	2.20.

Table 1 shows the geometric data for the saturated compounds, and Table 2 for the unsaturated. The results are also presented graphically in Figures 2 and 3. The RHF/6-31G* and the MP2/6-31+G* values are given for CP (CSi), CC, and PY (SiY) bond lengths. The CPC (CSiC) angles depend only on the ring geometries. Most compounds have C_{2v} symmetry, and only some hydroxy and amino compounds are distorted to C₂.

The MP2 values, which should be the more reliable, show almost the behavior described above. The CP and CSi bonds are all shorter in the unsaturated compounds than in their saturated counterparts. The difference in CP bond lengths is 0.05 ± 0.01 Å and for CSi a fairly constant 0.04 Å. The C–C bond lengths are particularly long (1.631 Å) for X = F, but more normal for X = H (1.521 Å), and show the reverse trend to the CP (1.733 for X = F, 1.805 for X = H) bond lengths. Similarly, there is a pronounced lengthening of the C=C bond in the unsaturated rings. For the phosphorus compounds they

range from 1.327 to 1.381 Å (for X = H and F, respectively) and from 1.347 to 1.380 Å for the silicon analogs with the same ligands.

There is only one published X-ray structure for a 1*H*-phosphirenium cation. The 1-(diisopropylamino)-1-(1,2-diphenyl-2-chloroethylene)-2,3-diphenyl-1*H*-phosphirenium cation exhibits C–P bond lengths of 1.730 and 1.732 Å (MP2: 1.724 Å) and a C=C bond length of 1.36 Å (MP2: 1.364 Å for the 1,1-diamino-phosphirenium cation).

The neutral 1-chloro-2phenyl-3-*tert*-butylphosphirene shows bond lengths C–P = 1.820 Å and C=C = 1.229 Å (C–P–C angle 41.8°).³² Its C=C double bond is much shorter than those in the charged structures.

3.2. Stability and Aromaticity. 3.2.1. Ring Strain. The ring strain energy in three-membered rings can be estimated by the isodesmic reaction shown in Scheme 3a.

The concept of bond separation energies as a measure of the destabilization of the rings was proposed by Hehre, Radom, Pople, and Schleyer^{33,34} and extended by Chesnut³⁵ who concludes that energies from bond separation energies provide one measure of the extent of stabilization resulting from cyclic conjugation (aromaticity) or destabilization (antiaromaticity) as well as all other types

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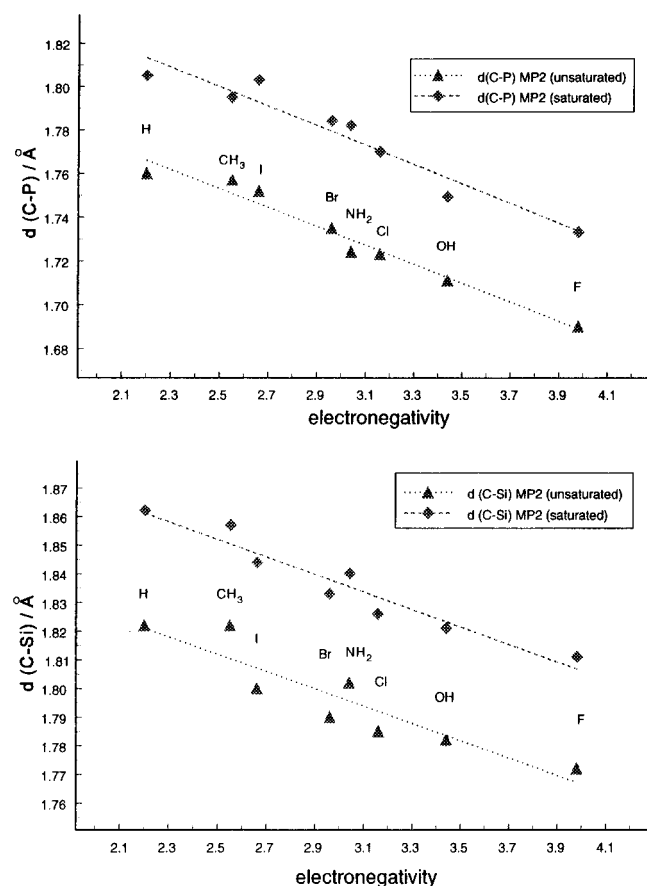
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Table 3. Ring Strain Energies as Obtained by the Isodesmic Reactions Shown in Scheme 3a (HF = HF/6-31G*//HF/6-31G*; MP4 = MP4SDTQ/6-31+G*//MP2/6-31+G*)

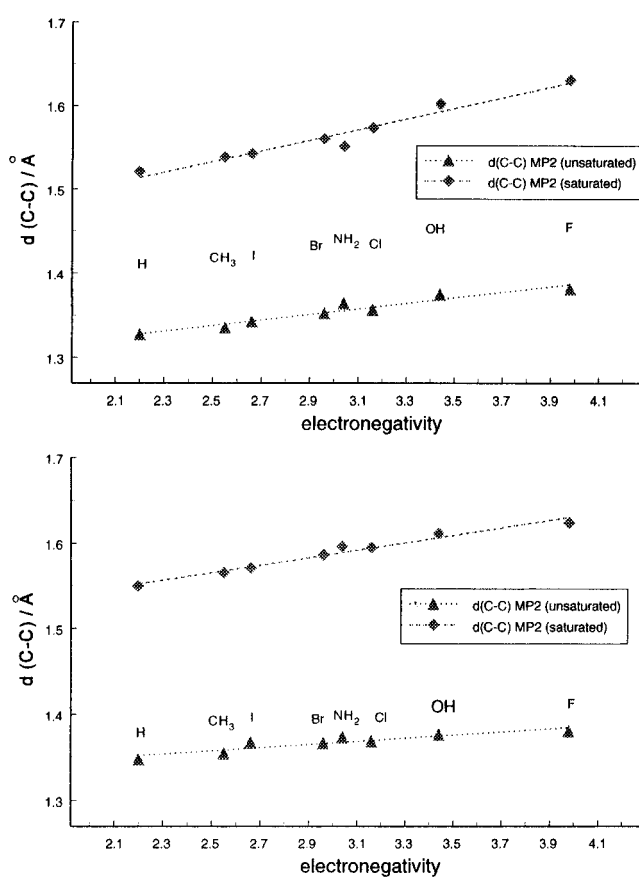
Y	P						Si					
	HF			MP4			HF			MP4		
	(CH ₂) ₂ PY ₂ ⁺	(CH) ₂ PY ₂ ⁺	Δ	(CH ₂) ₂ PY ₂ ⁺	(CH) ₂ PY ₂ ⁺	Δ	(CH ₂) ₂ SiY ₂	(CH) ₂ SiY ₂	Δ	(CH ₂) ₂ SiY ₂	(CH) ₂ SiY ₂	Δ
F	-35.56	-36.75	1.18	-29.36	-34.68	5.32	-38.68	-33.57	-5.11	-33.72	-31.93	-1.79
OH	-32.60	-33.69	1.08	-26.37	-31.88	5.50	-35.95	-29.10	-6.85	-30.50	-27.17	-3.33
Cl	-26.58	-31.54	4.95	-18.93	-26.95	8.02	-35.63	-32.03	-3.6	-27.63	-27.95	0.32
NH ₂	-28.28	-29.84	1.55	-21.84	-27.99	-6.14	-30.82	-25.21	-5.61	-25.42	-22.99	-2.43
Br	6.38	4.54	1.83	-18.25	-27.35	9.09	-48.95	-42.64	-6.31	-27.46	028.74	1.28
I	-21.61	-28.66	7.04	-10.35	-21.01	10.66	-32.91	-30.35	-2.56	-25.52	-26.92	1.4
CH ₃	-24.36	-31.50	7.13	-18.19	-27.93	9.73	-29.73	-33.23	3.5	-22.86	-29.71	6.85
H	-21.79	-30.67	8.87	-53.71	-65.23	11.52	-30.37	-29.53	-0.84	-23.33	-25.98	2.65

	(CH ₂) ₂ CH ₂	(CH) ₂ CH ₂	Δ
H			
HF	-20.51	-44.15	23.64
MP4	-18.87	-41.00	22.13

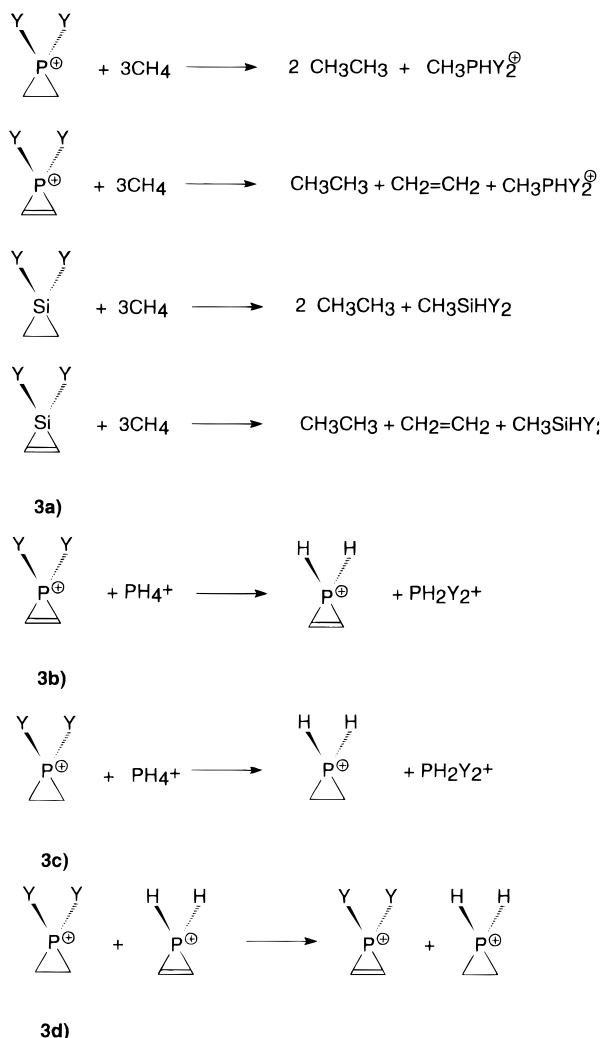
**Figure 2.** Dependence of bond length C-P or C-Si on the electronegativity of the substituent for saturated and unsaturated rings. Top: $d(C-P)$ in disubstituted 1*H*-phosphirenium cations and 1*H*-phosphiranium cations. Bottom: $d(C-Si)$ in disubstituted silacyclopropenes and silacyclopropanes.

of nonclassical interactions. In the following we will refer to destabilization as “strain” although there may be many factors combining to destabilize the system.

The strain is higher in double bonded three-membered rings than in single bonded ones because of the larger inherent bond angle at sp^2 carbon atoms. Reaction 3a is thus more exothermic for the double bonded ring. This is illustrated by the calculated bond-separation energies for cyclopropane and cyclopropene, which differ by about 22 kcal/mol (see Table 3). This high energy difference can be lowered by aromatic stabilization. For the phosphorus compounds, the more electronegative the substituent on phosphorus, the smaller the difference. The

**Figure 3.** Dependence of C-C bond length on the electronegativity of the substituent for saturated and unsaturated rings. Top: $d(C-C)$ in disubstituted 1*H*-phosphirenium cations and 1*H*-phosphiranium cations. Bottom: $d(C-C)$ in disubstituted silacyclopropenes and silacyclopropanes.

difference in strain energy, Δ , changes from $\Delta = 5.3$ kcal/mol for $Y = F$ to $\Delta = 9.7$ kcal/mol for $Y = CH_3$ (MP4 values; $\Delta = 8.0$ kcal/mol for hydrogen). There are three major deviations from the linear dependence of the bond-separation energies on the electronegativity of Y . The first $Y = H$ is to be expected for the first element of any series. For $Y = NH_2$, the two donor amino-groups interact more strongly with the C_{sp^2} -P bonds in the unsaturated system than with the less strained C_{sp^3} bonds of the saturated ring. This leads to a preferential donor (NH_2)-acceptor (three-membered ring) additional stabilization of the unsaturated ring. The almost planar structures of the NH_2 -substituents and their orientation relative to the ring bonds (see Figure 5) are indicative of

Scheme 3. Isodesmic Reactions Used to Interpret Relative Energies^a


^a For a discussion of the individual reactions, see text.

Table 4. Energies for the Reaction Schemes 3b and 3c. The Analogous Reactions Were Carried Out for the Silacyclopropanes and Silacyclopropenes. (HF = RHF/6-31G*/RHF/6-31G*; MP4 = MP4SDTQ/6-31+G/MP2/6-31+G*; for basis sets used for bromine and iodine see text)**

	F	OH	Cl	NH ₂	Br	I	CH ₃
	(CH) ₂ PY ₂ ⁺						
HF	+5.83	+2.82	+6.23	+2.24	-35.8	+3.98	-1.07
MP4	+6.40	+3.26	+9.92	+2.40	+7.14	+5.54	+1.18
	(CH) ₂ PY ₂ ⁺						
HF	-1.86	-4.97	+2.31	-5.08	-42.8	+2.15	-2.81
MP4	+0.19	-2.76	+6.41	-2.98	+4.71	+4.67	-0.61
	(CH) ₂ SiY ₂						
HF	+1.46	+3.97	+1.76	+5.85	-38.0	+2.12	-3.20
MP4	-0.19	+3.44	+3.98	+5.79	+2.42	+3.40	-1.85
	(CH) ₂ SiY ₂						
HF	-2.80	-2.02	-0.99	+1.08	-43.5	+0.39	+1.14
MP4	-4.63	-2.54	+1.66	+0.71	+1.05	+2.15	+2.35

these interactions. The extra stability of 1,1-dimethyl-1-silacyclopropane relative to the unsaturated analog is a consequence of low torsional strain in the CH₂-SiMe₂ ring bonds. The barrier (HF/6-31G*) for rotation of a methyl group in SiM₄, for instance, is only 1.5 kcal/mol, compared to 4.3 kcal/mol in neopentane. This effect is adequate to explain the ca. 5 kcal/mol preferential stability of the saturated silicon ring.

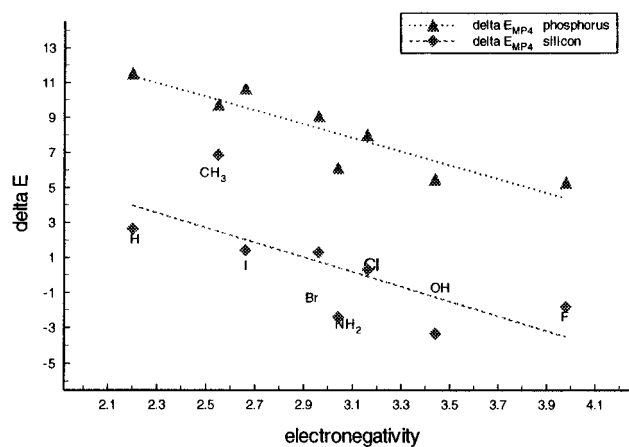


Figure 4. MP4SDTQ/6-31+G**/MP2/6-31G* ring strain energies as obtained by the isodesmic reactions shown in Scheme 3a.

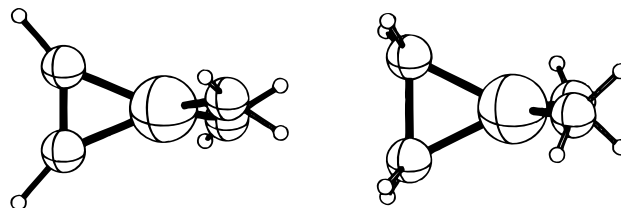


Figure 5. Structures of (CH)₂P(NH₂)₂⁺ and (CH)₂P(NH₂)₂⁺.

The silicon compounds show similar tendencies, but here some unsaturated structures are even more stabilized, so that their bond separation energies lie below those for the saturated ones. This is unexpected since hyperconjugation is usually stronger in cations than in neutral species.

3.2.2. Stabilization by Electronegative Ligands.

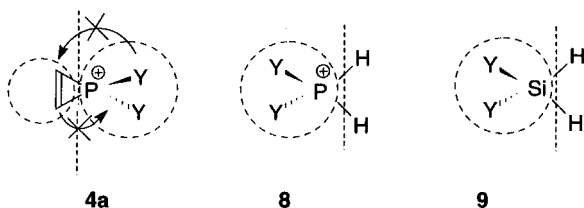
NBO Analysis. Isodesmic reaction 3a, however, gives energies in which a number of effects are combined. We therefore attempted to isolate π -conjugation effects by using reactions 3b and 3c. However, the results, shown in Table 4, give no clear trends. Here also several different contributions determine the calculated energies. Most of the reactions are slightly exothermic.

If, however, the ions **8** or **9** in the isodesmic reactions 3b and 3c are stabilized by their substituents Y to a similar extent as the three-membered rings, the results from Table 4 are consistent.

To understand this behavior better, Weinhold and Reed's Natural Population Analysis (NPA),³⁶ incorporated in GAUSSIAN94 has been used to analyze the orbital interactions within the ring systems.

We carried out an NBO analysis for all the calculated structures and for the ions in Schemes 3b and 3c (See Scheme 4). The interactions between the CC double bond (or the CC single bond) and phosphorus (silicon) were turned off by deleting the relevant Fock-matrix elements, thus destabilizing the system. The summation over all these deletions is the destabilization energy caused by neglect of these interactions. Table 5 lists the destabilization energies going from fluorine to hydrogen for all structures. These change from 115.1 kcal/mol for (CH)₂PF₂⁺ to 63.7 kcal/mol for (CH)₂PH₂⁺, a decrease of $\Delta = 51.4$ kcal/mol, but only from 54.2 kcal/mol for (CH)₂-

(36) NBO 4.0; Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, 1994.

Scheme 4. Interactions (symbolized by the arrows and the dashed lines) Turned Off in the NBO Analysis**Table 5. Destabilization Energies Obtained from the NBO Analysis for the Three-Membered Rings**

Y	(CH) ₂ PY ₂ ⁺	(CH) ₂ PY ₂ ⁺	(CH) ₂ SiY ₂	(CH) ₂ SiY ₂
F	115.11	54.22	73.97	32.29
OH	105.09	48.88	70.24	30.87
Cl	91.61	46.76	72.19	35.03
NH ₂	94.92	40.34	67.38	29.94
Br	88.42	44.96	68.71	38.35
I	77.56	41.81	71.11	36.87
CH ₃	69.24	37.54	56.63	27.77
H	63.72	29.48	51.53	22.09
δ_{stab} between F and H	51.39	24.74	22.44	10.20

Table 6. Destabilization Energies Obtained from the NBO Analysis for the Ions 8 and 9 (Scheme 4)

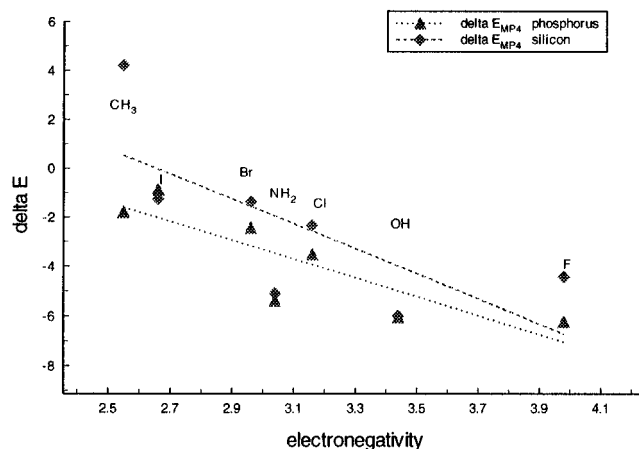
Y	(Y) ₂ ⇌ P(H ₂) ⁺	(Y) ₂ P ⇌ (H ₂) ⁺	(Y) ₂ ⇌ Si(H ₂)	(Y) ₂ Si ⇌ (H ₂)
F	81.69	2.10	62.43	1.23
OH	86.68	1.99	55.32	1.28
Cl	76.34	2.31	58.89	1.53
NH ₂	73.93	1.91	45.89	1.27
Br	68.59	2.58	58.78	1.96
I	45.34	2.42	42.78	1.53
CH ₃	36.58	2.92	24.79	1.32
H	2.04	2.04	1.13	1.13
δ_{stab} between F and H	79.65	≈0	61.30	≈0

PF₂⁺ to 29.5 kcal/mol for (CH₂)₂PH₂⁺ (Δ = 24.7 kcal/mol) as expected going from the unsaturated to the saturated species. The double bond interacts more strongly with the p-type σ^* -orbital than the single bond. The values for the silicon compounds are much lower (Δ = 22.4 kcal/mol for (CH)₂SiY and Δ = 10.2 kcal/mol for (CH)₂SiY) as proposed for uncharged species.

The same is true for the ions used to define reactions 3b and 3c (see Table 6). Here one has to delete the interaction between the fragment Y₂P⁺ (Y₂Si) and the fragment "H₂". This causes a change in destabilization energy of Δ = 79.7 kcal/mol (Δ = 61.3 kcal/mol). The other interaction between H₂P⁺ (H₂Si) and "Y₂" does not play a significant role (columns 2 and 4 in Table 6).

It follows from these considerations that the stabilization effects caused by the ligands Y largely determine the overall energy change in the isodesmic reactions. Because the destabilization energies are of the same order of magnitude on both sides of the reaction schemes, it is not clear to what extent the overall reaction energy is determined by the ligand–ligand interactions and how much it is caused by hyperconjugation and σ^* -aromaticity.

3.2.3. Eliminating the Effect of Ring Strain. The previous sections show that when trying to identify for σ^* -aromaticity it is necessary to use isodesmic reactions that (a) eliminate the effects of substituents, which means comparing the single and the double bonded species with the same ligand Y, and (b) eliminate the

**Figure 6.** MP4SDTQ/6-31+G*/MP2/6-31+G* σ^* -aromatic stabilization energies derived from isodesmic reactions 3d.**Table 7. Energies for the Isodesmic Reactions 3d: (HF = RHF/6-31G*/RHF/6-31G*; MP4 = MP4SDTQ/6-31+G*/MP2/6-31+G*)**

	F	OH	Cl	NH ₂	Br	I	CH ₃
(CH) ₂ PY ₂ ⁺ /(CH) ₂ PY ₂ ⁺							
HF	-7.69	-7.79	-3.92	-7.32	-7.05	-1.83	-1.74
MP4	-6.21	-6.02	-3.50	-5.37	-2.43	-0.86	-1.79
(CH) ₂ SiY ₂ /(CH) ₂ SiY ₂							
HF	-4.26	-5.98	-2.75	-4.77	-5.46	-1.72	+4.34
MP4	-4.45	-5.99	-2.33	-5.08	-1.37	-1.25	+4.20

effect of different ring strains for the single and the double bonded species.

One such reaction is shown in Scheme 3d. There are saturated and unsaturated phosphacycles (or silacycles) on both sides of this reaction. The rings also carry the same ligands Y on both sides. Although this reaction assures that the ring strain in the saturated compound is not affected by the substituents, the measured effect is a fair approximation of the change in σ^* -aromaticity that causes the unsaturated systems to be stabilized over the saturated relative to the systems with Y = H. The greatest stabilization (-6.2 kcal/mol) is found for the most electronegative element fluorine and the smallest (-0.9 kcal/mol) for iodine (see Figure 6 and Table 7). Once again, the amino group deviates from the general trend for the phosphorus rings. The energy dependence on ligand electronegativity for the silicon rings is almost linear, ranging from a stabilization of -4.5 kcal/mol for Y = F to a destabilization of +4.2 kcal/mol for Y = CH₃. Note that these energies are changes relative to Y = H and not the absolute stabilization due to σ^* -conjugation.

4. Conclusions

The proposal that substituted 1*H*-phosphirenium cations and substituted silacycloprenes with substituents Y (F, Cl, Br, I, OH, NH₂, CH₃, H) show a stabilization caused by the p-type σ^* -orbital on phosphorus or silicon antibonding to the ligands Y interacting with the double bond in the ring has been tested. σ^* -Aromaticity influences the geometries of the systems dependent on the electronegativity of Y. These systems were compared to the analogous saturated rings, which exhibit a similar but weaker interaction to π_{CH_2} orbitals on the ring. *Ab initio* calculations at the RHF/6-31G* and MP4/6-31+G* levels show a lengthening of the carbon–carbon bonds which is stronger for the single bonds than the double bonds. There is also a shortening of the C–P (C–Si)

bonds. Both geometry changes are more significant for phosphorus than for silicon.

Three-membered rings are strained structures. Isodesmic reactions (Scheme 3a) that open the rings are a measure of this ring strain energy. Double bonds in the ring increase this strain. If the rings are stabilized, e.g., by σ^* -aromaticity, the difference between the ring strain energy of the saturated to the unsaturated ring is reduced. This difference is 22.1 kcal/mol for the system cyclopropane/cyclopropene, which exhibits no stabilization, only 5.3 to 8.0 kcal/mol for the phosphorus and even -1.8 to -0.8 kcal/mol for the silicon compounds. According to this definition, the 3-silacyclopropenes are hyperstable olefins.

An NBO analysis was used to investigate the interactions of the various fragments XY_2 ($X = P, Si$; $Y =$ ligand) with the double or single bonds and for the same fragments used in ions in isodesmic reactions (Schemes 3b and 3c). There is a similar decrease in the interaction energy between fragment XY_2 and the C–C (C=C) bond in the three-membered rings as with the “H₂” rest in the ion that masks the cyclic conjugation effects.

Thus, a reaction eliminating all steric and ligand inherent substituent effects and all effects caused by ring strain was used (Scheme 3d). The energies of these reactions are direct values for the stabilization going from single bonded to double bonded rings with the same substituents Y. The more electronegative the ligand the more exothermic the reaction. Some ligands deviate from

these almost linear dependencies, especially NH₂, I, and CH₃.

Overall, σ^* -aromaticity is found to be a weak but significant effect stabilizing the substituted 1*H*-phosphirenium cations and the silacyclopropenes over their saturated analogs. The saturated rings profit from similar p-orbital interactions as the unsaturated rings but to a lesser extent. Although we have no way to define the absolute value of the stabilization, it is reasonable to attribute the difference in Δ values (Table 3) between carbon and phosphorus rings (14 kcal/mol) to σ^* -aromaticity. This arbitrariness assigns zero stabilization to the carbon rings and leads to the conclusion that the 1*H*-phosphirenium cations enjoy aromatic stabilization energies of 14–20 kcal/mol ($Y = H$ to F) and the silacyclopropenes 19–27 kcal/mol ($Y = CH_3$ to F).

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Supporting Information Available: GAUSSIAN archive entries for RHF/6-31G* calculations (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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