Articles

Ab Initio Theoretical Investigation of the Formation of Phosphirenylium Ions from 1-Halo-1*H*-phosphirenes[1]

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The formation of phosphirenylium ions from fluoro- and chlorophosphirenes was studied by ab initio calculations at various theoretical levels up to CCSD(T)/6-31+G*. To study the substituent effects, 13 sets of differently substituted halophosphirenes and phosphirenylium ions were optimized using HF and MP2 methods and the 6-31+G* basis set. The energies were improved by MP4-(SDTQ) and CCSD(T) single-point calculations using the same basis set. The obtained reaction energies vary between 114 and 209 kcal/mol depending on the halogen at phosphorus and the substitution at the ring carbons. The effect of liquid SO_2 as a solvent was approximated by calculations of discrete complexes of solvent molecules and solutes. It is found that this solvent stabilizes the phosphirenylium cation by 18 kcal/mol. The electronic structures of the molecules and the ions were studied by NBO analyses. The P−X bonds are found to be of highly ionic character and can be described as interactions between phosphirenylium and halide ions. The aromatic character of the phosphirenylium ion is shown to be based on a three-center two-electron bond of π-type and the resonance energy is assessed by calculation of a homodesmotic reaction and is estimated to be 38 kcal/mol.

1. Introduction

According to the Hückel rule, the smallest possible aromatic structure is a three-membered ring with a π-system consisting of three p-orbitals perpendicular to the ring plane and occupied by two π-electrons.[2] In the case of hydrocarbons, this aromatic ion is well-known since its first synthesis by Breslow in 1957.[3,4] It was intensely investigated by NMR spectroscopy,[5] mass spectrometry,[6] and X-ray structure analysis.[7] The special interest in this species results from its aromaticity, the interesting bonding properties, and the fact that it is one of the most stable carbenium ions. The first theoretical investigations dealt with the aromaticity of this ion by means of Hückel−MO theory,[8] and early ab initio calculations proved the parent cyclopropenylium ion to be the lowest energy structure on the $C_3H_3^+$ potential energy surface.[9] Just recently, the resonance energy of this ion

Scheme 1
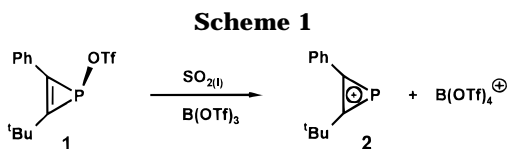
was assessed by high-level ab initio calculations.[10]

In contrast to the cyclopropenylium ion, which has been known for a long time, its phosphorus analogue was first synthesized just recently. It can be obtained by addition of the strong Lewis acid $B(OTf)_3$ to a solution of the 1*H*-phosphirene **1** in liquid SO_2 (Scheme 1).[11] To the best of our knowledge, this is the only example of a free, persistent phosphirenylium ion, and also, only one stable transition-metal complex of this species is published.[12]

Before this generation of the ion **2**, substituted phosphirenylium ions were only noticed in the mass spectra of 1*H*-phosphirenes[13] and cyclooligomers of phosphaalkynes,[14] and the parent ion was found in ion gas-flow reactions of PH_n^+ and P_n^+ cluster ions in the mass spectrometer.[15] Several attempts to generate this ion in

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solution failed; e.g., treatment of 1-halo-1*H*-phosphirenes with salts containing non-nucleophic anions such as PF_6^- [16] or BPh_4^-[17] was unsuccessful. The synthesis of the (trifluoromethyl)sulfonate-substituted phosphirene **1**[18] was one key step in the generation of **2**. As the solventdependence of the ^{31}P NMR resonance[19] indicates, the P−O bond is already very weak. The expected phosphorus chemical shift of the phosphirenylium ion was previously predicted by IGLO calculations[20] and was confirmed by experimental values. A second important effect is the extremely strong Lewis acidity of the used $B(OTf)_3$[21] and its high affinity to bond a further (trifluoromethyl)sulfonate ion under formation of $B(OTf)_4^-$.[22] A final influence was the application of liquid SO_2 as solvent, which has been well-known for its strong heterolysis supporting properties for almost 100 years.[23]

While the experimental work finally succeeded in generating a persistent phosphirenylium ion, there is still not much theoretical knowledge available about this system. Only the parent ion was calculated and was shown to be the lowest energy structure on the $C_2H_2P^+$ potential energy surface,[24] and this result has been confirmed by the latest studies.[25] But no investigations about the formation, reaction energies, and aromaticity were performed so far. An explanation is still lacking for the great difficulties in generating this ion, which was quite unexpected from our experience with the cyclopropenylium system.

Hence, the aim of the present paper is to get detailed information about the phosphirenylium ion and the energetic situation of its formation by the use of ab initio theory. We were interested in the molecular and electronic structures and in the aromaticity of the ions. Further, we studied substituent effects on the stabilization of the phosphirenylium ions, and finally, we investigated the influence of the solvent SO_2 on the reaction.

2. Computational Methods

We investigated sets of phosphirenylium ions and fluoro- and chlorophosphirenes of 13 different substitution patterns including the parent system. As substituents, we studied methyl, silyl, cyano, hydroxy, and amino groups and some combinations of two different substituents. As a model for the solvation of the phosphirenylium ions, we calculated complexes with one and two SO_2 molecules attached to the cation. This method was already used to study the solvent effects in the case of anions and was shown to be very useful.[26] All structures were fully optimized at the HF/6-31+G* and MP2/6-31+G* level of theory, and stationary points were characterized as real minima by subsequent frequency calculations.[27] We chose the 6-31+G* basis set,[28] containing one set of diffuse sp-orbitals at each heavy atom, to account for the more diffuse electron distribution in the anions,[29] phosphorus compounds, and the long-distance interactions of the solvent complexes. To improve the energies, we performed MP4/6-31+G* single-point calculations at the MP2-optimized structures to include a higher level of electron correlation. For the parent systems and some cases in which strange effects in the MP4 energies were noticed, we enhanced the level to CCSD(T)/6-31+G* to improve the reliability of the results, but most of the structures were too large to apply this level of sophistication. All relative energies were corrected for zero-point vibrational energy (ZPE). For economic reasons, the ZPE's were calculated at the HF level only and were scaled by a factor of 0.89.[30] The bonding situation, especially that of the phosphirenylium ion, was studied by NBO analysis.[31] For these calculations we used the MP2 structures but the HF wave function, because in this way we can obtain information about bond orbital interactions by a simple second-order perturbation approach. Further, we get the natural charges[32] and the Wiberg bond indices[33] based on the NAO Fock matrix from the NBO analysis, which will be used in the discussion as well.

3. Results and Discussion

Structures. As expected and already reported by Nguyen et al.,[34] optimization of the parent halophosphirenes results in structures of C_s symmetry with a strongly pyramidalized phosphorus atom. By substitution at the carbon atoms, this symmetry is lowered to C_1 in most cases. Especially in the symmetrically substituted **13a**, a remarkable difference between the two amino groups is found, while **13b** is almost of C_s symmetry. These contrasting results cannot be explained so far. The structural parameters of the substituted phosphirenes **4a,b** to **15a,b** show some distinct differences

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
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Table 1. Selected Bond Lengths (Å) of 1-Halo-1*H*-phosphirenes and Phosphirenylium Ions Obtained from MP2/6-31+G* Optimization

Structure		P1 - X2	P1 - C3	P1 - C4	C3 - C4	C3 - R5	C4 - R6
	3a	1.679	1.796	1.796	1.324	1.083	1.083
	3b	2.122	1.806	1.806	1.319	1.083	1.083
	3c	-	1.737	1.737	1.353	1.086	1.086
	4a	1.679	1.801	1.794	1.326	1.483	1.084
	4b	2.133	1.810	1.804	1.321	1.481	1.084
	4c	-	1.753	1.730	1.361	1.472	1.086
	5a	1.686	1.799	1.799	1.327	1.485	1.485
	5b	2.144	1.807	1.807	1.323	1.483	1.483
	5c	-	1.745	1.745	1.369	1.475	1.475
	6a	1.658	1.808	1.800	1.330	1.408	1.084
	6b	2.101	1.819	1.810	1.326	1.406	1.084
	6c	-	1.750	1.740	1.362	1.402	1.088
	7a	1.674	1.826	1.785	1.331	1.863	1.084
	7b	2.122	1.839	1.794	1.326	1.864	1.084
	7c	-	1.768	1.723	1.363	1.926	1.086
	8a	1.675	1.814	1.814	1.338	1.865	1.865
	8b	2.122	1.825	1.825	1.333	1.865	1.865
	8c	-	1.752	1.752	1.374	1.919	1.919
	9a	1.673	1.774	1.808	1.327	1.343	1.083
	9b	2.129	1.780	1.818	1.324	1.340	1.082
	9c	-	1.745	1.735	1.370	1.293	1.086
	10a	1.676	1.784	1.784	1.333	1.354	1.354
	10b	2.142	1.789	1.789	1.330	1.351	1.351
	10c	-	1.744	1.744	1.387	1.302	1.302
	11a	1.683	1.780	1.809	1.325	1.349	1.485
	11b	2.147	1.786	1.818	1.322	1.346	1.483
	11c	-	1.749	1.749	1.372	1.299	1.474
	12a	1.685	1.787	1.783	1.334	1.359	1.082
	12b	2.154	1.790	1.791	1.331	1.355	1.082
	12c	-	1.769	1.712	1.382	1.305	1.085
	13a	1.694	1.779	1.779	1.337	1.379	1.381
	13b	2.198	1.779	1.779	1.337	1.375	1.375
	13c	-	1.748	1.748	1.394	1.317	1.317
	14a	1.692	1.784	1.788	1.335	1.367	1.487
	14b	2.168	1.787	1.794	1.332	1.363	1.485
	14c	-	1.763	1.726	1.387	1.309	1.478
	15a	1.690	1.795	1.772	1.331	1.372	1.357
	15b	2.175	1.799	1.777	1.329	1.367	1.353
	15c	-	1.774	1.732	1.384	1.309	1.307
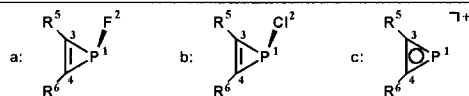
compared to the parent system (Table 1). One general observation is that the P−C bonds of the chlorine compounds are always longer than those of their fluorine analogues, while the C−C double bonds are shorter in the chlorine case. From this bond length it could be supposed that in the fluorine compounds the three-membered ring already picks up some aromatic character of the phosphirenylium structure, which could be explained by the stronger polarization of the P−F bond.

The distance between the halogen and the phosphorus atom can be used as an indicator for the strength of this bond. The values of 1.673 Å (**3a**) and 2.122 Å (**3b**) for the parent compounds are located somewhere in the middle between the longest and shortest found distances. The shortest bonds are found for the cyano-substituted

phosphirenes **6a,b**, while the longest distances are obtained for the bis(amino)phosphirenes **13a,b**. This is in very good agreement with the assumption that amino substitution should stabilize the phosphirenylium ion and hence should reduce the strength of the P−X bond.

In the structural parameters of the three-membered ring the dependence on the substitution pattern is less obvious. To study the influence of the substituent type, only the symmetrically substituted structures should be treated. Again, the parent compounds show approximately average values if only the P−C bond length is treated. The methyl-substituted structures **5a,b** have only slightly longer P−C bonds than **3a,b**, but silyl substitution as in **8a,b** leads to a noticeable elongation of these bonds. In contrast to this, hydroxy groups

Table 2. Selected Bond Lengths (Å) and Bond Orders of the Alkenes 16−19 from ab Initio Calculations

Structure	d (C−C)	d (C−R)	b.o. (C−C)	b.o. (C−R)
16 (SiH₃)	1.348	1.872	2.005	0.810
17 (CH₃)	1.342	1.500	1.987	1.042
18 (H₃Si, SiH₃)	1.357	1.878	1.986	0.809
19 (H₃C, CH₃)	1.347	1.502	1.945	1.037

Table 3. Bond Interactions (kcal/mol) of the Alkenes 16−19 Obtained from NBO Analyses Showing Hyperconjugation of the π-System

donor → acceptor[a]	16	17	18	19
C1−C2 → X3−H	3.8	3.4	3.1	3.3
C1−C2 → X4−H			2.9	3.3
X3−H → C1−C2	1.5	4.7	1.7	4.6
X4−H → C1−C2			1.3	4.6

[a] Numbering of atoms:

X: C, Si
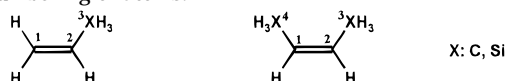
(10a,b) afford a slight, amino substitution (13a,b), a stronger shortening of the P−C bonds. The values of the C−C double bond show that the structural parameters of the ring obviously give no information about the tendency to aromatize by cleavage of the P−X bond. The longest C−C bond is found for silyl substitution (8a), which afforded the longest P−C bonds too. But in the chlorine case amino substitution (13b) leads to the longest C−C bond, while the P−C bonds are the shortest of all symmetrically substituted phosphirenes. The silyl substitution in 8b results in only the second longest C−C double bond but nevertheless confirms the effect of the two silyl groups. The substituent effect of silyl groups on C−C double bonds was already systematically investigated,[35] especially to explain the stabilizing β-silicon effect in carbenium ions.[36] This effect is ascribed to the ability of silicon to undergo hyperconjugation with the appropriate π-systems. Unfortunately, mainly the energies of silylated species were studied, and the influence on the C−C bond distance is not discussed so far. Hence, we calculated silylethylene (16) and *cis*-1,2-bis(silyl)-ethylene (18) and compared the bond lengths to propene (17) and *cis*-2-butene (19).[37] Indeed, we find that the C−C distance in the silylated compounds is slightly longer than in the methyl-substituted structures (Table 2). It could be supposed that this effect is due to hyperconjugation, but the calculated bond interactions obtained from NBO analysis result only in a very small amount of hyperconjugation, which is even larger in the methyl-substituted structures than in the silyl compounds (Table 3). This is in good agreement with the statement of Kutzelnigg that hyperconjugation is not important in neutral species.[38] A better explanation can be given from the natural atomic charges of the system

(35) (a) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462. (b) Wiberg, K. B.; Laidig, K. E. *J. Org. Chem.* **1992**, *57*, 5092.

(36) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(37) All structures were optimized at the MP2/6-31+G* level of theory to be comparable to the results obtained for the phorphirenes.

(38) Kutzelnigg, W. *Einführung in die Theoretische Chemie*; Verlag Chemie: Weinheim, 1978; Vol. 2, p 328.

Table 4. Natural Atomic Charges and Dipole Moments of Alkenes 16−19

	16	17	18	19
C1[a]	−0.72	−0.20	−0.67	−0.23
C2[a]	−0.37	−0.45	−0.67	−0.23
X3[a]	1.09	−0.68	1.08	−0.67
X4[a]			1.08	−0.67
μ	0.70	0.40	0.70	0.24

[a] Numbering of atoms as indicated in Table 3.

(Table 4). These charges show that in the silylated structures the C−Si bond is extremely polarized, resulting in an increased dipole moment and a higher negative charge at the carbons of the double bond. This should lead to a stronger electrostatic repulsion being responsible for the stretched double bonds.

The structures optimized for the phosphirenylium ions show some characteristic changes compared to their neutral precursors. In all cases, the C−C bond is remarkably stretched and the P−C bonds are notably shortened, which is in perfect agreement with the assumption of an aromatic system. Again, the dependence of the atomic distances on the substitution pattern shows no clear trends. The parent ion affords the shortest distances for all bonds. The longest P−C bonds of the symmetric structures are found for the silylated 8c while amino substitution (13c) results in the longest C−C bond. Interesting effects are found for the change of atomic distances between ring carbons and substituents upon ion formation. For the cyano group, almost no effect is found, and the bond to the methyl moieties is slightly shortened while the C−Si bond is noticeably stretched. Distinct shortening is found for hydroxy and amino substitution, which points to a participation of heteroatom lone pairs in the aromatic π-system. This assumption is further confirmed by the planarity of the amino and hydroxy groups, affording ions of C_s and C_{2v} symmetry, respectively. In the case of silyl substitution (7c, 8c) the possible hyperconjugation leads neither to a shortening of the C−Si bond nor to a visible elongation of the C−C bond. Instead, the long C−Si bond could be explained by the positive charge of the ring, resulting in a repulsive electrostatic force on one hand and the necessity to share the electron-donor capabilities of the ring carbons between two positive centers (Si and P) on the other hand. For the silyl groups, it seems that mainly the electronegativity is the driving force for the structures and not orbital effects such as hyperconjugation. This conclusion is parallel to the findings of Wiberg for substituent effects in ethyl, vinyl, isopropyl, and cyclopropyl systems.[35b]

Bonding Considerations. To investigate the bonding situation in phosphirenes and especially the phosphirenylium ion we performed NBO analyses. A lot of information is obtained from the Wiberg bond indices (Table 5). The first discovery is the low bond index of approximately 0.5 for the P−F bond, which is known to be a very strong bond. The reason for this seeming contradiction is that the Wiberg bond index only represents the covalent part of the bond. This leads to the conclusion that in the P−F bond there is a large portion of ionic bonding present. The bond index of about 0.8 for the P−Cl bond is much closer to a covalent single bond, obviously showing less ionic character.

The natural atomic charges give a further confirmation for the strong polarization of the P−F bond. The fluorine

Table 5. Wiberg Bond Indices of 1*H*-Phosphirenes and Phosphirenylium Ions[a] from NBO Analysis

structure	P1−X2	P1−C3	P1−C4	C3−C4	C3−R5	C4−R6
3a	0.537	0.945	0.945	1.961	0.887	0.887
3b	0.801	0.949	0.949	1.966	0.884	0.884
3c		1.222	1.222	1.670	0.858	0.858
4a	0.531	0.924	0.948	1.923	1.023	0.885
4b	0.785	0.930	0.951	1.924	1.024	0.882
4c		1.178	1.253	1.619	1.046	0.858
5a	0.525	0.928	0.928	1.887	1.019	1.019
5b	0.770	0.934	0.934	1.886	1.020	1.020
5c		1.210	1.210	1.572	1.039	1.039
6a	0.555	0.865	0.919	1.879	1.067	0.883
6b	0.841	0.871	0.926	1.881	1.069	0.881
6c		1.128	1.206	1.605	1.082	0.854
7a	0.538	0.916	0.946	1.942	0.731	0.883
7b	0.804	0.921	0.951	1.948	0.724	0.879
7c		1.200	1.245	1.655	0.645	0.857
8a	0.540	0.918	0.918	1.926	0.727	0.727
8b	0.807	0.924	0.924	1.933	0.720	0.720
8c		1.220	1.220	1.643	0.651	0.651
9a	0.534	0.927	0.936	1.874	1.013	0.888
9b	0.791	0.936	0.938	1.871	1.020	0.885
9c		1.124	1.302	1.540	1.151	0.861
10a	0.527	0.919	0.919	1.833	0.991	0.991
10b	0.771	0.927	0.927	1.823	0.997	0.997
10c		1.192	1.192	1.455	1.124	1.124
11a	0.523	0.940	0.936	1.839	0.997	1.020
11b	0.765	0.949	0.939	1.832	1.004	1.021
11c		1.166	1.278	1.480	1.132	1.043
12a	0.520	0.911	0.981	1.793	1.138	0.888
12b	0.754	0.925	0.984	1.783	1.147	0.885
12c		1.057	1.413	1.426	1.352	0.864
13a	0.507	0.945	0.945	1.738	1.084	1.084
13b	0.694	0.963	0.963	1.711	1.092	1.092
13c		1.185	1.185	1.308	1.301	1.301
14a	0.514	0.917	0.960	1.781	1.117	1.017
14b	0.736	0.930	0.967	1.768	1.125	1.018
14c		1.081	1.362	1.340	1.332	1.037
15a	0.510	0.926	0.970	1.763	1.101	0.979
15b	0.725	0.937	0.981	1.742	1.111	0.988
15c		1.114	1.301	1.346	1.338	1.112

a) Substitution pattern as indicated in Table 1.

carries a charge of about −0.7 with a charge at phosphorus of about +1.2, while the chlorine charge is only −0.4, causing a charge at phosphorus of +0.8. Interestingly, the influence of the carbon substitution on the charges at phosphorus and the halogens is very limited.

The deviations of the P−X bond indices upon substitution are more characteristic, even though they are only of small magnitude. While the parent phosphirenes **3a**,**b** show a somewhat average bond index, the strongest bonds are found for cyano substitution (**6a**,**b**) and the lowest indices are that of the bis(amino) compounds **13a**,**b**. Also, cyano substitution (**6a**,**b**) affords the weakest P−C bond while amino groups (**13a**,**b**) cause the strongest bonds, but for the C−C double bond again no clear trend can be found. Interesting observations are made for the bonds between ring carbons and substituents. Only for protons and silyl groups are bond indices of noticeably less than 1.0 obtained. The C−Si bond obviously is of low covalent character. In fact, the neutral species show strongly positive charges for silicon (+1.1) and highly negative charges at carbon (−0.7 to −0.8),

resulting in a remarkable polarization of the bond and enhancement of its ionic character. In contrast, for methyl moieties bond indices slightly greater than 1.0 are observed, which is a consequence of slight hyperconjugation. The largest effects are found for amino substituents resulting in bond indices up to 1.15 (**12b**) for the C−N single bond. Here, a lone pair at nitrogen of almost p-type interacts with the π-bond between the two ring carbons causing typical conjugation effects (Table 6). A similar interaction is observed for the hydroxy group.

Additionally, the C−C double bond is weakened by an interaction with the P−X single bond. This interaction is particularly strong in the case of **13a**,**b** where the lone pairs of the two amino groups already interact with the C−C π-bond. The reason for this effect is the high p-character of the orbital at phosphorus participating in the P−X σ-bond, which enables the π-system to donate electrons into the σ*-orbital. An extreme exception from this bonding situation is found for **10a**. Here the NBO analysis locates a three-center two-electron (3c-2e) bond of π-character between P1, C3, and C4. Because the p-orbital of phosphorus is needed for this bond to a great extent, a stronger participation of d-functions (32%) is necessary to form the P−F bond.

Upon P−X bond cleavage and ion formation there take place a few remarkable changes in atomic charges and bond indices. Compared to the chlorophosphirenes, the positive charge at phosphorus is enhanced, as expected. In contrast, in all fluoro compounds this atom carries a higher positive charge than in the ions. But, because the halogen atoms of the phosphirenes do not carry full charges of −1.0, the phosphirenylium ring must pick up some positive charge. At least in the case of ion formation from the fluorophosphirenes, this is done by the ring carbons, which reduce their negative charge significantly. A clear descent of this negative charge is observed from fluoro via chloro to the ionic compounds, no matter what the substitution pattern looks like.

Notable changes are found for the bond indices too (Table 5). The first observation is that the P−C bonds show significantly enhanced values of about 1.2, in some cases even 1.3, indicating a remarkable participation of the π-system in bonding. As a consequence, the C−C double bonds are weakened, which is indicated by bond indices between 1.3 (**13c**) and 1.7 (**3c**). This is a clear expression of the aromatic character of the ions, because it shows that there are bonding interactions of π-type between all three ring atoms. In the case of **13c** there should take place an almost perfect delocalization according to the bond indices of the three ring bonds. It can be noticed that the bonds between hydroxy and amino groups and the ring carbons show strongly enhanced bond indices in the phosphirenylium ions compared to the neutral species, so they seem to interact even better with the delocalized π-system of the ions.

The NBO analyses of the phosphirenylium ions further reveals that there are 3c-2e bonds present that would explain the delocalization of π-electrons. The bond is formed by three orbitals of almost pure p-type standing perpendicular to the ring plane. The so formed π-orbital is occupied almost exactly by two electrons that are completely delocalized, proving the aromaticity of the ionic structures.

Energies of Ion Formation. From the assumption of its aromatic character, the ion can be expected to be

Table 6. Bond Interactions (kcal/mol) of Moieties with the C−C Double Bond in 1-Halo-1*H*-Phosphirenes

structure[a]	donor → acceptor	energy	structure[a]	donor → acceptor	energy
6a	C - C(π) → C - N(π*)	18.0	**12b**	N(LP) → C - C(π*)	59.9
6b	C - C(π) → C - N(π*)	18.2	**13a**	N(LP) → C - C(π*)	42.8/36.9[b]
9a	O(LP) → C - C(π*)	47.7	**13b**	N(LP) → C - C(π*)	39.2
9b	O(LP) → C - C(π*)	48.6	**14a**	N(LP) → C - C(π*)	51.3
10a	O(LP) → C - C - C(π*)	39.4	**14b**	N(LP) → C - C(π*)	52.4
10b	O(LP) → C - C(π*)	39.7	**15a**	N(LP) → C - C(π*)	44.8
11a	O(LP) → C - C(π*)	43.1		O(LP) → C - C(π*)	44.8
11b	O(LP) → C - C(π*)	43.9	**15b**	N(LP) → C - C(π*)	45.7
12a	N(LP) → C - C(π*)	58.5		O(LP) → C - C(π*)	36.1

a) Substitution pattern as indicated in Table 1. b) Amino groups are different.

Table 7. Relative Energies of 1-Halo-1*H*-phosphirenes (kcal/mol) from Calculations at Various Levels of Theory

structure[a]	HF/6-31+G*[b]	MP2/6-31+G*[c]	MP4/6-31+G*[c,d]	ΔE[e]
3a	−195.51	−193.62	−194.51	0.0
3b	−141.37	−148.61	−154.57	0.0
4a	−187.61	−185.13	−186.05	8.4
4b	−134.23	−141.17	−147.08	7.5
5a	−180.30	−177.37	−178.37	16.1
5b	−127.67	−134.48	−140.39	14.2
6a	−212.12	−207.88	−208.66	−14.2
6b	−159.08	−163.18	−169.02	−14.4
7a	−190.25	−188.09	−198.41	−3.9
7b	−136.59	−140.24	−159.36	−4.8
8a	−186.21	−184.03	−184.49	10.0
8b	−133.06	−140.91	−146.35	8.2
9a	−189.01	−188.27	−185.87	8.6
9b	−137.44	−140.38	−146.08	8.5
10a	−181.06	−175.82	−176.41	18.1
10b	−126.73	−131.09	−136.78	17.8
11a	−181.02	−176.93	−177.60	16.9
11b	−127.61	−133.17	−138.85	15.7
12a	−176.45	−171.61	−172.28	22.2
12b	−123.09	−127.38	−133.07	21.5
13a	−156.98	−151.08	−152.19	42.3
13b	−104.46	−107.83	−113.85	40.7
14a	−168.89	−163.97	−164.84	29.7
14b	−116.29	−120.81	−126.63	28.0
15a	−167.93	−162.28	−183.59	10.9
15b	−114.60	−118.38	−144.72	9.9

a) Substitution pattern as indicated in Table 1. b) Corrected for zero-point vibration by scaled ZPE. c) Corrected for zero-point vibration by scaled ZPE obtained from HF/6-31+G* calculation. d) MP4(SDTQ) single point calculation on MP2 optimized structures. e) Changes of the relative energy with respect to the parent compounds. Stabilization of the ions causes positive values.

quite stable, as is found for the cyclopropenylium ion. Of course, a heterolytic bond cleavage in the gas phase, as treated by ab initio calculations, usually is a highly endothermic process. A first glance at the calculated energies of the investigated heterolysis clearly shows that in all cases the 1-halo-1*H*-phosphirenes are much more stable than the resulting ions (Table 7).

In the following text, we will analyze the effects on these energies in detail. To find out something about the reliability of our calculations, we calculated structures and energies at various levels of theory and checked the trends of the results. Compared to the HF energy, the MP2 calculation always reduces the stability of the neutral molecule by up to 6 kcal/mol. In the case of the fluoro compounds, the MP2 method seems to overestimate this destabilization, which is corrected by the MP4-(SDTQ) calculations except for structures **7a**, **9a**, and

15a. The chloro compounds show a clearly different behavior. A continuous increase of the stability of the phosphirenes is found from HF via MP2 to MP4 calculations. The MP4 energies are about 6 kcal/mol lower than the MP2 results, and only **7b** and **15b** deviate significantly from this trend. To check the convergence of the computed energies, we performed CCSD(T)/6-31+G* calculations[39] on the MP2 structures of the parent system and obtained relative energies of −195.9 (**3a**) and −154.5 kcal/mol (**3b**). While the fluorophosphirene is found to be slightly more stable at this level, the chloro compound shows almost exactly the same value as at the MP4 level. Additionally, the total energies of the parent compounds only show differences in the range of a few millihartrees (**3a**) and a few tenths of millihartrees (**3b**, **3c**) between the MP4 and the CCSD(T) results.[40] Although this is not a final proof for the reliability of the MP4 values because both methods are not based on the variational principle, it indicates that at least in our case the MP4 results can be taken as a good approximation to the much more costly but usually more accurate CCSD(T) calculations.

The relative energies of the parent system of −194.5 and −154.6 kcal/mol indicate two very stable structures. The P−F bond turns out to be on average 39 kcal/mol more stable than the P−Cl bond. The great stability of the phosphirenes makes it obvious that the aromaticity of **3c** stabilizes the ion not enough to make its formation a favorable process in the gas phase. To get a crude estimation of the resonance energy in **3c**, we calculated the fully saturated phosphirane system (**20**) too (Table 8).

For the phosphiranes **20a,b**, we find relative energies of −223.4 and −187.1 kcal/mol, respectively. **20a** is 28.9 kcal/mol more stable than **3a** with respect to the ions, and for the chlorine structure **20b** this difference is even larger (32.5 kcal/mol). If this energy difference would be the resonance energy (ring strain is neglected) the stabilization should be equal for both fluorine and chlorine compounds. The deviation from this assumption can be explained by our previous findings that the fluorophosphirene already picks up some aromatic character. From the difference of these two values we obtain the resonance energy of −3.6 kcal/mol for the neutral **3a**. Of course, this interpretation of the rather crude assumption is only valid if other structural influences in the phosphiranes are of minor importance, but the qualitative statements seem to be clear and correct.

(39) CCSD(T) is known to give more reliable results in the case of strong electron correlation effects: (a) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Lee, T. J.; Scuseria, G. E.; Rice, J. E.; Scheiner, A. C.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1987**, *139*, 134.

(40) Total energies at the MP4(SDTQ)/6-31+G* and CCSD(T)/6-31+G* level of theory are as follows. MP4(SDTQ): **3a**, −517.607 25; **3b**, −877.598 62; **3c**, −417.664 94. CCSD(T): **3a**, −517.603 91; **3b**, −877.598 99; **3c**, −417.664 89.

Table 8. Relative Energies of Phosphirane Structures 20a,b (kcal/mol) with Respect to Phosphiranyl Cation 20c from Calculations at Various Levels of Theory

20a: 20b: 20c:

| structure	HF/6-31+G*	ZPE	E_{rel}	MP2/6-31+G*	E_{rel}	MP4/6-31+G*	E_{rel}
20a	−518.221 64	34.24	−226.46	−518.770 68	−224.05	−518.823 83	−223.44
20b	−878.260 16	33.81	−175.08	−878.759 80	−182.89	−878.821 39	−187.14
20c	−418.438 16	31.72		−418.783 55		−418.833 99	

A more elaborate method to assess the stabilization energy is the calculation of the homodesmotic reaction[41] displayed in Scheme 2.

This pattern was suggested by Radom et al.[9] and recently was used by Glukhovtsev et al.[10] to calculate the resonance energy of the cyclopropenylium ion. To get energies comparable with those of Glukhovtsev, we calculated the energies of the homodesmotic reaction by use of G2 theory[42] and obtained a resonance stabilization of 38.4 kcal/mol.[43] The value obtained for the cyclopropenylium ion is 59.0 kcal/mol, which shows that the less perfect overlap of the phosphorus p-orbital with the carbon p-orbitals leads to a smaller but still significant stabilization. Furthermore, a comparison with the above-estimated resonance energy of 32.5 kcal/mol gives some additional evidence that at least the order of magnitude of the true stabilization will be in the range of 30−40 kcal/mol.

We tried to find out which influences can support the investigated reaction further and thus studied substituent effects. For this purpose, we calculated derivatives of **3a−c** with methyl, silyl, cyano, hydroxy, and amino groups attached to the C−C double bond (Table 7).

In the case of one methyl group (**4**), a stabilization of about 8 kcal/mol is calculated. The introduction of a second methyl moiety (**5**) leads to a reduction of the reaction energy of a little less than twice this value. A second observation is that the fluorophosphirene is slightly more destabilized than the chloro compound. This seems to be a general trend for all substituents.

A substituent closely related to the methyl group is the silyl moiety. Both substituents are well established to stabilize cations in β-position. Usually, this effect is larger for silyl substitution, but surprisingly in the monosubstituted system (**7**) we even find a stabilization of the neutral species. On the other hand, the doubly substituted system **8** shows a stabilization of 8−10 kcal/mol for the cation, which contradicts the findings for **7**. A careful look at the relative energies obtained for **7a,b** shows that there is an inconsistency between the MP2 and MP4 values. According to the MP2 energies, the single silyl group would be stabilizing by 5−8 kcal/mol. We supposed that the MP4 method produces an artifact in this case and thus performed single-point calculations at the CCSD(T)/6-31+G* level, which afforded relative energies of −190.0 (**7a**) and −149.5 kcal/mol (**7b**). This result leads to the expected conclusion that the silyl group acts slightly stabilizing on the ions. The MP4

Scheme 2
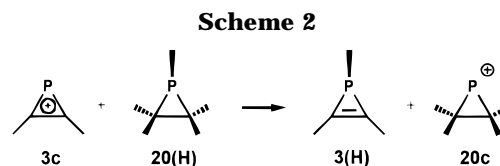
method obviously produces a large error in this case that we are not able to explain. Nevertheless, if the erroneous MP4 value is substituted by the CCSD(T) or MP2 result, all the usual trends that we obtained for the other substitution patterns are fulfilled again.

For the cyano group we find a destabilization of the cation of 14 kcal/mol that is no artifact. In contrast to the silyl group, this effect was not unexpected because this moiety is well-known to be electron withdrawing, which destabilizes cations.

Substituents that are expected to stabilize the phosphirenylium ion are hydroxy and amino groups. Indeed, we find that one hydroxy group (**9**) affords a stabilization of about 8 kcal/mol, which is of comparable magnitude to the effect of the methyl group. Unexpectedly, the stabilization by two hydroxy groups is more than twice as strong (18 kcal/mol). In most other cases it is found that the total stabilization is a little less than the sum of the single substituent effects.

While hydroxy moieties give a moderate stabilization, the influence of the amino group is quite strong. A single amino group (**12**) reduces the energy of the phosphirenylium ion by 22 kcal/mol and a second amino substituent (**13**) increases this effect up to 42 kcal/mol. In combination with a methyl group (**14**), again the effect is found to be approximately additive, resulting in an energy change of 28−30 kcal/mol. For the system containing an amino and hydroxy moiety (**15**) it seems from the MP4 energies that the stabilizing effects counteract each other. An inconsistency between MP2 and MP4 similar to the inconsistency for **7a,b** can be noticed. According to the MP2 values, a stabilization of approximately 30 kcal/mol is obtained, which would be about the sum of the single effects. It seems that the MP4 method produces an artifact. Unfortunately, this system was too large to be calculated at the CCSD(T) level, but instead of **15** we checked the singly substituted **9** by this method. The CCSD(T)/6-31+G* calculations resulted in energies of 187.3 (**9a**) and −146.0 kcal/mol (**9b**), which indicates the MP4 value of the fluoro compound to be too small, but for **9b** MP4 and CCSD(T) values are almost equal. This shows that the MP4 method may be erroneous for the systems containing hydroxy groups as it is very likely in **15**. In such cases, it seems to be better to treat the MP2 values, if no CCSD(T) calculations can be performed.

The investigation of the substituent effects results in the finding that substitution by two amino groups lowers the reaction energy by up to 42 kcal/mol, but the process still remains highly endothermic. So far, we treated only

(41) (a) George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121. (b) George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. (c) George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

(42) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(43) Total energies at the G2 level are as follows: **3c**, −417.809 39; **20(H)**, −419.922 29; **3(H)**, −418.685 16; **20c**, −418.985 41.

Table 9. Relative Energies of Halo- and (Trifluorosulfonyl)phosphines 21−23 (kcal/mol) with Respect to the Ions from Calculations at Various Levels of Theory

structure	HF[a]	MP2[b]	MP4//MP2[b]	CCSD(T)//MP2[b]
H$_2$P−OTf (**21**)	−169.17	−177.79		
H$_2$P−F (**22**)	−249.67	−245.80	−246.29	−245.87
H$_2$P−Cl (**23**)	−200.13	−204.97	−211.04	−208.82

[a] Relative energy in (kcal/mol) corrected by ZPE. [b] Relative energy in (kcal/mol) corrected by ZPE obtained from HF/6-31+G* calculation.

the substitution at the ring carbons. If the bond energy of the phosphorus moiety can be reduced further, the reaction energy will decrease too. The substituent used in the first successful formation of a phosphirenylium ion was the (trifluoromethyl)sulfonate (OTf) group. Because of the size of this moiety we investigated the heterolysis of the parent phosphinyl (trifluoromethyl)sulfonate (**21**) and compared the results to fluoro- (**22**) and chlorophosphine (**23**), respectively. The (trifluoromethyl)sulfonate anion itself can be calculated at relatively little computational expense because of its C_{3v} symmetry. The assumed C_s symmetry for **21** leads to a stationary point affording one imaginary frequency corresponding to an inner rotation. From the low imaginary frequency of 18i cm^{-1} we decided not to reoptimize the structure because we did not expect a substantial change in energy. Compounds **22** and **23** were optimized in C_s symmetry and are proved to be real minima. While for the (trifluoromethyl)sulfonyl system the highest computational level was MP2/6-31+G*, we tested the reliability of the results for the halophosphines with calculations up to CCSD(T)/6-31+G*//MP2/6-31+G* level (Table 9).

As for the phosphirenes, it is found that the energies of the fluoro compounds can be approximated by the MP2 method quite well and that MP4 and CCSD(T) values show only a very small difference. In contrast, the chloro compound affords much less agreement between the different methods. The stability of **23** is continuously increased up to the MP4(SDTQ) calculation, but the CCSD(T) value lies between the MP2 and MP4 energies. At the most accurate level (CCSD(T)), the difference of the P−X bond strength is computed to be 37 kcal/mol for this system, which is comparable to the average value of 39 kcal/mol in the case of the phosphirenes. On the other hand, the reaction energies of 246 and 209 kcal/mol for the halophosphines are notably higher than that of the phosphirenes, which again shows the stabilization of the phosphirenylium ion. If we now treat the phosphinyl (trifluoromethyl)sulfonate **21**, we find a remarkable reduction of the reaction energy by 68 kcal/mol with respect to **22**, proving the low stability of the P−OTf bond. If we use the bond strength difference between the P−F and the P−OTf bond, we can estimate that the heterolysis energy of a bis(amino)phosphirenyl (trifluoromethyl)sulfonate would still be 84 kcal/mol. This led us to the already expected conclusion that two other factors play a decisive role: Lewis acid and the solvent. The complexation of the anion by a Lewis acid is not part of this paper and may be discussed elsewhere, but the solvation effects that are specific for the phosphirene system will be reported here.

Solvent Effects. In a recent study, we investigated the solvation of fluoride and chloride anions in liquid SO$_2$ and found out that it is necessary to calculate discrete complexes of solvents and solute.[26] The generation of a
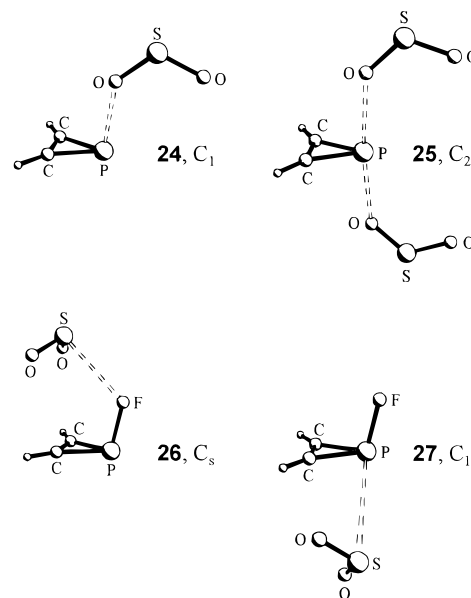

Figure 1. Structures of SO$_2$ complexes of the phosphirenylium (**24** and **25**) ions and the 1H-phosphirenes (**26** and **27**) obtained from geometry optimization at the MP2/6-31+G* level of theory.

persistent phosphirenylium ion necessarily required the use of liquid SO$_2$ as solvent, and only in this specific solvent was the ion stable.[11] From our previous studies, we know that this solvent is able to stabilize anions to a large extent. Now we report about the stabilization of the phosphirenylium cation by SO$_2$ complexation.

At first, we optimized the singly and doubly complexed phosphirenylium ions **24** and **25** (Figure 1) with computational levels up to MP2/6-31+G*. For **24**, we considered two different complexation modes, complexation by the sulfur or one oxygen atom, but only for the latter was a stationary point obtained. We also started from geometries in which the ligand was placed above the center of the ring or even the C−C double bond. The sole obtained structure (**24**) shows only a contact between one oxygen and the phosphorus atom that is quite similar to the neutral phosphirenes. The second oxygen points away from the ring and is slightly distorted, resulting in C_1 instead of C_s symmetry. The P−O distance of 2.324 Å seems to be rather long, but the Wiberg bond index of 0.134 shows that a small amount of covalent bonding is present. The natural charge at phosphorus is unchanged (1.17), but ring carbons (−0.43) and the two protons (0.31) pick up some negative charge that is transferred from the SO$_2$ ligand. Of course, the complexation has a distinct impact on the structure of the ion. The P−C bonds are stretched to distances of 1.751 Å while the C−C bond is shortened to 1.339 Å. Thus, the contact to the solvent molecule seems to disturb the delocalization of the π-electrons of the ring.

The NBO analysis of **24** shows two donor−acceptor interactions between the two lone pairs at oxygen and the 3c-2e bond of the ion, resulting in stabilizing energy contibutions of 13 and 28 kcal/mol. A back-donation is not of noticeable magnitude. The calculated energy of the complex shows that **24** is stabilized by 15 kcal/mol compared to the parent ion (Table 10). Thus, the complexation is almost as effective as substitution by an amino group.

We optimized another complex **25** in which the phos-

Table 10.   Energies of SO₂–Phosphirenylium (24, 25) and SO₂–1H-Phosphirene Complexes (26 and 27) Calculated at Various Levels of Theory

structure	HF/6-31+G*	ZPE	E_{rel}	MP2/6-31+G*	E_{rel}
24	−964.482 18	23.50	−11.03	−965.346 32	−15.02
25	−1511.673 48	28.43	−20.33	−1513.063 18	−26.12
26	−1064.202 52	24.92	−3.45	−1065.268 04	−5.51
27	−1064.198 30	24.77	−0.96	−1065.263 38	−2.74
SO₂	−547.175 70	4.44		−547.698 39	

phorus atom is complexed by two SO₂ ligands. This structure is of C_{2v} symmetry, and as in **24**, the two SO₂ molecules are turned "outward" with the noncomplexing oxygen pointing away from the ring. The P–O distance of 2.515 Å is even longer than in **24**. The P–C bonds are further stretched (1.752 Å) and the C–C bond is further shortened (1.336 Å), but the differences between **24** and **25** are quite small while the changes compared to **3c** are significant. The obtained natural charges show that the phosphorus becomes slightly more positive (1.18), but again the charge transfer from the ligands, which is a little bit stronger in **25**, is compensated by the carbons (−0.44) and hydrogens (0.30). The covalent bonding between phosphorus and the oxygens is reduced, indicated by bond indices of 0.081, but the total amount of covalent bonding and of charge transfer in **25** is larger than in **24**. The NBO analysis of **25** reflects interactions of the two oxygen lone pairs with the 3c-2e bond causing stabilizing interaction energies of 11 and 12 kcal/mol for each ligand. Again, the single interactions are weaker than in **24**, but the effect of the sum is stronger. Thus, the complexation by two SO₂ ligands stabilizes the phosphirenylium cation by 26 kcal/mol.

To consider the effect of liquid SO₂ as a solvent on the heterolysis reaction, the solvation of the starting material must be taken into account as well. Hence, we optimized two different complexes of **3a** and a SO₂ ligand (Figure 1). The assumed complexation of the fluorine atom by one SO₂ molecule leads to structure **26**. MP2 optimization leads to an almost C_s symmetric geometry showing a weak contact of 2.879 Å between S and F while the HF method results in a C_1 structure. The two oxygens are placed above the ring carbons, but the distance of 3.312 Å between the atoms should result in almost negligible orbital interactions. This is confirmed by the NBO analysis, which locates a 3c-2e bond for the phosphirene unit that interacts very slightly with the S–O bonds of the ligand. Because of the long distances, the covalent interactions between the units are almost zero as is the charge transfer. This leads to the conclusion that almost exclusively van der Waals forces are active in this complex. Nevertheless, a remarkable stabilization energy of 5.5 kcal/mol is obtained.

In the second complex **27**, the phosphorus atom shows a contact of 3.764 Å to the sulfur, and again the oxygens are directed toward the carbons. The MP2 optimization provides a C_1 symmetric geometry, even though the HF/6-31+G* calculation resulted in C_s symmetry. It is worth noting that the optimization was started from an arrangement in which a P–O contact was preformed but resulted in the depicted structure of **27** only. It is not surprising that covalent, charge-transfer, and bond-orbital interactions are very small like in **26**. The calculated stabilization energy of 2.7 kcal/mol is even smaller than that of **26**.

If we approximate the solvent effect of the neutral species by adding up both types of complexation we get

a solvation energy of 8.2 kcal/mol. If we compare the solvation energies of the neutral phosphirene and the cation we obtain a difference of 17.9 kcal/mol that favors the ion formation. This is the energetic contribution of the solvent effect to the reaction energy originating from the stabilization of the cation only. To obtain the total reaction energy, the stabilization of the anion must be taken into account as well.

4. Conclusions

The influence of the substitution pattern and the solvent on structures and energies of 1H-phosphirenes and phosphirenylium ions have been investigated by means of ab initio theory. Furthermore, the bonding situation of these compounds and the aromaticity of the ion were studied.

For the 1-halo-1H-phosphirenes it is found that the P–X bond is strongly polarized, containing substantial ionic contributions, especially in the fluorine case. This bond can be described as an interaction of the π-system of the phosphirenylium cation with an electron pair of a halide anion. The phosphirenylium ion is shown to be aromatic, providing a perfectly delocalized π-system that forms a three-center two-electron (3c-2e) bond. Comparison of the heterolysis energies of phosphirenes **3** and phosphiranes **20** resulted in an estimated resonance energy of 32.5 kcal/mol for the parent phosphirenylium ion. From the calculation of a homodesmotic reaction (Scheme 2) a resonance stabilization of 38.4 kcal/mol is obtained. The stability of the P–X bond is dependent on the anion, showing that the P–F bond is 39 kcal/mol more stable than the P–Cl bond. From a comparison of halophosphines (**22** and **23**) and phosphinyl (trifluoromethyl)sulfonate (**21**), the P–OTf bond is found to be approximately 68 kcal/mol less stable than the P–F bond.

The substitution pattern at the ring carbons causes a remarkable impact on structures and relative energies of the phosphirenes. While a cyano group stabilizes the neutral species, silyl, methyl, hydroxy, and amino groups favor the cation. The effect of silyl substitution is surprisingly low, but as expected, the amino group causes the largest effect. Two amino groups stabilize the cation by about 40–42 kcal/mol. Nevertheless, the heterolysis reaction still remains an endothermic process in the gas phase.

Solvent effects were investigated by calculation of discrete complexes of solvent and solute molecules. The cation is stabilized by complexation at phosphorus by one or two SO₂ molecules. One oxygen of the ligand interacts with the phosphorus p-orbital of the 3c-2e bond, leading to a reduced delocalization of the π-electrons of the ring. The lowering of the heterolysis energy by SO₂ was estimated to be 18 kcal/mol.

If all energetic contributions of substituents at phosphorus and the ring carbons and the solvation are transferable, then a model system can be proposed that would be far too large to be calculated at the desired accuracy. If a bis(amino)phosphirenyl (trifluoromethyl)sulfonate in liquid SO₂ is treated by combining the energetic contributions of the singly studied effects, its reaction energy should still be about 66 kcal/mol. A more realistic approximation of the experimentally investigated system would be a phosphirenyl (trifluoromethyl)sulfonate containing two methyl groups for which a

reaction energy of 92 kcal/mol can be estimated. This shows that substitution and solvation of phosphirene and phosphirenylium cation is very important for the reaction energy. But additionally, a stabilization of the anion by complexation by a Lewis acid and solvation of the complex is inevitably necessary as well to obtain an exothermic reaction. This final conclusion may explain the great difficulties to prepare the phosphirenylium ion experimentally.

Supporting Information Available: Three tables containing detailed numerical information about natural bond orbital analyses, natural atomic charges and dipole moments, and total energies of phosphirenes and phosphirenylium ions. Cartesian coordinates of all optimized structures (20 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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