

In Search of Singlet Phosphinidenes

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We have examined singlet–triplet energy separations in different phosphinidenes (RP) substituted by first- and second-row elements, making use of ab initio molecular orbital theory. Our main purpose is to find out the substituents that particularly favor the singlet electronic state. The QCISD(T)/6-311++G(3df,2p) + ZPE level has been applied to small molecules and the CISD(Q) and QCISD(T) with the 6-311G(d,p) basis set for all species considered. We have identified few factors that come into play rendering the singlet phosphinidene more stable than the triplet. The parent phosphinidene, PH, has a triplet ground state lying 28 kcal/mol below the closed-shell singlet excited state. The triplet ground state is mainly favored when negative hyperconjugation is involved. In the boryl-, alkyl-, and silyl-substituted phosphinidenes, the triplet state remains by far the ground state. When the substituents have π -type lone pair electrons (i.e., $-NX_2$, $-PX_2$, $-OX$, $-SX$), the singlet state becomes stabilized by such an amount that both states have similar energies or even a change in ground state occurs. The most stabilized singlet ground states are attributed to PSF and PSCI. P and S have similar p-orbital sizes, making π -delocalization easier. Implantation of alkyl and/or amino groups in the β -position of amino- and phosphinophosphinidenes also contributes to a singlet stabilization. Bulky β -groups also destabilize the triplet state by a steric effect. From a practical viewpoint, amino ($P-NR_2$) and phosphino ($P-PR_2$) derivatives bearing large alkyl groups (R) are the most plausible and feasible targets for preparing phosphinidenes possessing a closed-shell singlet ground state.

1. Introduction

Phosphinidenes (R–P) are known as important transient species in phosphorus chemistry and can be stabilized through complexation with transition metal fragments.^{1–3} The preparation of phosphinidene–metal complexes and their use in organophosphorus syntheses have been elegantly developed by Mathey and co-workers.³ Due to their short lifetime and high reactivity, even under mild conditions, chemical properties of phosphinidenes have been deduced mainly from trapping or complexation experiments. Compared with the widely developed electron-deficient species such as carbenes,⁴ nitrenes,⁵ and silylenes,⁶ little is known, however, about the free monovalent and monocoordinated phosphorus species (RP).

It is useful to have a brief overview of some phosphinidenes which we further consider in our discussion. The electronic ground state of the parent phosphinidene (PH) is a triplet that is 22 kcal/mol⁷ more stable than the lowest-lying singlet state. This phosphinidene has also been detected in interstellar clouds⁸ and in planetary atmosphere.⁹ In the late 1960s, the first arylphosphinidene was detected by mass spectrometric techniques

performed on a cyclopolyphosphine.¹⁰ More recently, Carrié and co-workers¹¹ proposed that an arylphosphinidene is formed as an intermediate in the thermal decomposition of a 1,2,3,4-triazaphospholine.

Some amino- and phosphino-substituted phosphinidenes have been observed mostly as ligands in terminal phosphinidene complexes. The former have usually been prepared by thermal decompositions of aminophosphirane complexes according to the procedure presented by Mathey et al.¹² These authors argued that this rather facile reaction could proceed only through a stabilized low-lying singlet state of the aminophosphinidene moiety. Phosphinophosphinidene complexes have also been found.¹³ Fritz et al.¹⁴ showed that the alkyl-substituted phosphinophosphinidene $P-P(^tBu)_2$ can also be trapped by olefins or dienes to give the corresponding phosphiranes. The unprecedented formation of phosphiranes from olefins and dienes corresponds to the expected behavior of a singlet phosphinidene. Nevertheless, no information could be obtained by these research groups to establish the ground state of amino- and phosphinophosphinidenes.

During the last three years, different general approaches to generate phosphinidenes^{15–17} have been proposed, but in none of these experiments was a free

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Table 1. Total Zero-Point Vibrational (in Hartrees) and Relative (in kcal/mol) Energies of Simple Phosphinidenes

P-R	CISD(Q)/6-311G(d,p) ^a		QCISD(T)/6-311G(d,p) ^a		QCISD(T)/6-311++G(3df,2p) ^a		ZPE ^b	
	<i>E</i> (T) ^c	ΔE (T-S)	<i>E</i> (T) ^c	ΔE (T-S)	<i>E</i> (T) ^c	ΔE (T-S)	S	T
PH	-341.389 89	-33.3	-341.392 10	-32.0	-341.424 02	-28.0	3.2	3.2
PLi	-348.259 97	-40.8	-348.266 51	-40.6	-348.306 23	-42.3	0.6	0.6
PBH ₂	-366.740 50	+18.8	-366.743 76	+21.8	-366.791 78	+23.5	11.2	11.7
PCH ₃	-380.603 23	-32.4	-380.608 59	-29.5	-380.668 71	-26.0	21.2	21.7
PNH ₂	-396.630 49	-3.1	-396.637 69	-1.4	-396.716 41	-1.2	15.8	15.0
POH	-416.420 79	-20.5	-416.487 17	-18.3	-416.582 37	-16.9	8.1	8.0
PF	-440.481 18	-33.4	-440.488 19	-30.3	-440.594 53	-27.5	1.2	1.1
PSiH ₃	-631.616 44	-34.3	-631.619 68	-29.3	-631.683 97	-25.6	15.1	15.1
PPH ₂	-682.850 28	-6.9	-682.854 63	-3.9	-682.937 40	-1.2	10.7	10.7
PSH	-739.081 74	-12.4	-739.086 70	-10.6	-739.183 96	-6.1	5.7	5.5
PCI	-800.475 83	-31.6	-800.480 26	-28.9	-800.589 05	-25.5	0.7	0.7

^a Based on (U)MP2/6-31G(d,p) optimized geometries. Core orbitals are frozen. A negative value for ΔE (T-S) indicates a triplet ground state. ^b Zero-point energies obtained from (U)HF/6-31G(d,p) vibrational wavenumbers and scaled by 0.9. ^c $\langle S^2 \rangle \leq 2.025$ in UHF wave functions for triplets; total energies of singlets are omitted.

phosphinidene actually detected. The mechanism of these reactions remains to be established through careful kinetic and/or spectroscopic studies. Thiohydroxyphosphinidene (HS-P) was shown by Terlouw et al.¹⁸ to be a stable species in the gas phase which survives during a neutralization-reionization mass spectrometric experiment.

Only recently, Gaspar et al.¹⁹ have been successful in detecting mesitylphosphinidene using ESR spectroscopy and have thus established for the first time the existence of a free arylphosphinidene in its triplet state. Nevertheless, according to Mathey,²⁰ all these postulated transient phosphinidenes in their triplet state exhibit an inherent lack of reactivity; for this reason, it is more interesting to generate phosphinidenes in a singlet state in order to achieve higher and cleaner reactivity. A way of shedding more light on this problem is to examine systematically different types of substituents attached to the phosphorus atom. It is known that, in the case of carbenes and nitrenes, π -donor substituents in the α -position exert dramatic effects on their singlet-triplet energy separation. Therefore, we have been interested in searching phosphinidenes having a closed-shell singlet ground state using ab initio molecular orbital calculations. In this paper, we present a detailed account of the behavior of first-row and second-row substituents with respect to this property. Our main purpose is to evaluate as accurately as possible the singlet-triplet energy gaps and to find out which substituents stabilize the singlet state.

2. Theoretical Methods

Ab initio molecular orbital calculations were carried out using the Gaussian 92²¹ and Molcas 3²² program packages on a IBM RISC 6000 computer. The equilibrium structures were located using analytical energy derivatives at both HF and MP2 levels with the 6-31G(d,p) basis set. The unrestricted formalism (UHF,²³ UMP²⁴) was used for the triplet state. Relative singlet-triplet energies were obtained at the (U)MP2/6-31G(d,p) optimized geometry and uniformly estimated from configuration interaction calculations with single and double excitations from HF references and corrections for unlinked quadruple excitations (CISD(Q)).²⁵ The core orbitals are kept frozen in CI calculations. We also performed quadratic configuration interaction calculations with perturbative correction for triple excitations (QCISD(T)),²⁶ with the larger 6-311++G(3df,2p) basis set²⁷ for the following small molecules: PH, PLi, PF, PCI, PBH₂, PCH₃, PNH₂, POH, PSH, PSiH₃, and PPH₂. For larger

substituents, the smaller basis sets 6-311++G(d,p)²⁸ and 6-311G(d,p)²⁹ were used, with or without triple excitation contributions in the quadratic CI method. Zero-point vibrational contributions to relative energies were obtained from (U)HF/6-31G(d,p) frequency calculations and scaled by 0.9 to account for systematic overestimation. All the energetic data can be found in Tables 1 and 2.

The spin contamination in UHF references for triplet states is rather small. A presentation of geometrical parameters for the phosphinidenes considered is illustrated in Figure 1. Correlation diagrams showing the singlet-triplet relationships are shown in Figures 2 and 3.

3. Results and Discussion

We have divided the substituents considered into three main groups: diatomic species, substituents without lone pairs, and substituents containing elements with lone pairs. Each group will be examined separately, and a general discussion will be presented at the end with the aid of some correlation diagrams. We have not considered in this work the unsaturated substituents containing a π -system, such as vinylphosphinidene (H₂C=CH-P). The closed-shell singlet state of these molecules cannot be treated properly by single-reference calculations. In what follows, ΔE (T-S) designates the singlet-triplet energy separations; its value is negative when the triplet

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Table 2. Total Zero-Point Vibrational (in Hartrees) and Relative (in kcal/mol) Energies of Phosphinidenes

P-R	CISD(Q)/6-311G(d,p) ^a			QCISD(T)/6-311G(d,p) ^a			ZPE ^b	
	E(S)	E(T) ^c	$\Delta E(T-S)$	E(S)	E(T) ^c	$\Delta E(T-S)$	S	T
PBF ₂	-564.991 75	-565.030 67	-24.3	-565.030 54	-565.049 07	-11.5	5.9	6.0
PBCl ₂	-1284.947 80	-1284.984 47	-23.3	-1284.964 39	-1284.987 96	-14.6	5.0	5.2
PC ₂ H ₅	-419.758 55	-419.809 34	-31.3	-419.776 74	-419.823 80	-28.9	38.5	39.2
PCF ₃	-677.748 43	-677.806 81	-36.6	-677.782 69	-677.835 34	-33.8	8.8	9.0
PCCl ₃	-1757.705 16	-1757.754 49	-30.9	-1757.704 85 ^d	-1757.752 50 ^d	-29.7	5.5	5.7
PNF ₂	-594.609 69	-594.609 41	+0.3	-594.637 33	-594.633 48	+1.8	5.9	5.5
PNCl ₂	-1314.651 67	-1314.649 52	+1.0	-1314.682 59	-1314.667 91	+8.9	4.3	4.0
PNH(CH ₃)	-435.826 36	-435.826 56	-0.8	-434.842 81	-435.839 68	+1.2	33.2	32.5
PN(CH ₃) ₂	-475.024 73	-475.024 80	-0.8	-475.048 71	-475.044 95	+1.7	50.2	49.5
PPHF	-781.932 27	-781.928 01	+2.5	-781.951 82	-781.940 14	+7.1	7.9	7.7
PPF ₂	-881.016 29	-881.025 28	-6.1	-881.045 83	-881.046 04	-0.6	4.6	4.1
PPHCl	-1141.920 11	-1141.922 14	-1.3	-1141.935 36	-1141.930 74	+2.8	7.1	7.0
PPCl ₂	-1600.989 41	-1600.995 83	-4.5	-1601.010 85	-1601.009 68	+0.3	3.1	2.7
PPH(CH ₃)	-722.057 25	-722.061 53	-2.7	-722.073 00	-722.072 12	+0.6	28.6	28.6
PP(CH ₃) ₂	-761.274 06	-761.273 54	+0.2	-761.297 25	-761.291 50	+3.7	46.2	46.1
PPH(NH ₂)	-738.077 66	-738.082 58	-2.5	-738.095 39	-738.049 60	+1.0	21.7	22.2
PP(NH ₂) ₂				-793.360 39	-793.346 17	+8.2	33.9	33.2
PPHPH ₂	-1024.301 00	-1024.307 02	-3.7	-1024.315 78	-1024.316 58	-0.4	17.2	17.4
PSiF ₃	-928.973 17	-929.028 77	-34.9	-929.006 31	-929.054 65	-30.3	4.0	3.9
PSiCl ₃	-2008.894 52	-2008.943 80	-30.9				4.0	4.0
PSF	-838.126 64	-838.104 05	+14.3	-838.297 06	-838.264 52	+20.2	2.3	2.2
PSCl	-1198.135 50	-1198.119 36	+10.0	-1198.155 00	-1198.129 03	+16.3	1.6	1.6

^a Based on (U)MP2/6-31G(d,p) optimized geometries. Core orbitals are frozen. A negative value for $\Delta E(T-S)$ indicates a triplet ground state. ^b Zero-point energies obtained from (U)HF/6-31G(d,p) vibrational wavenumbers and scaled by 0.9. ^c $\langle S^2 \rangle \leq 2.025$ in UHF wave functions for triplets. ^d QCISD/6-311++G(d,p) level.

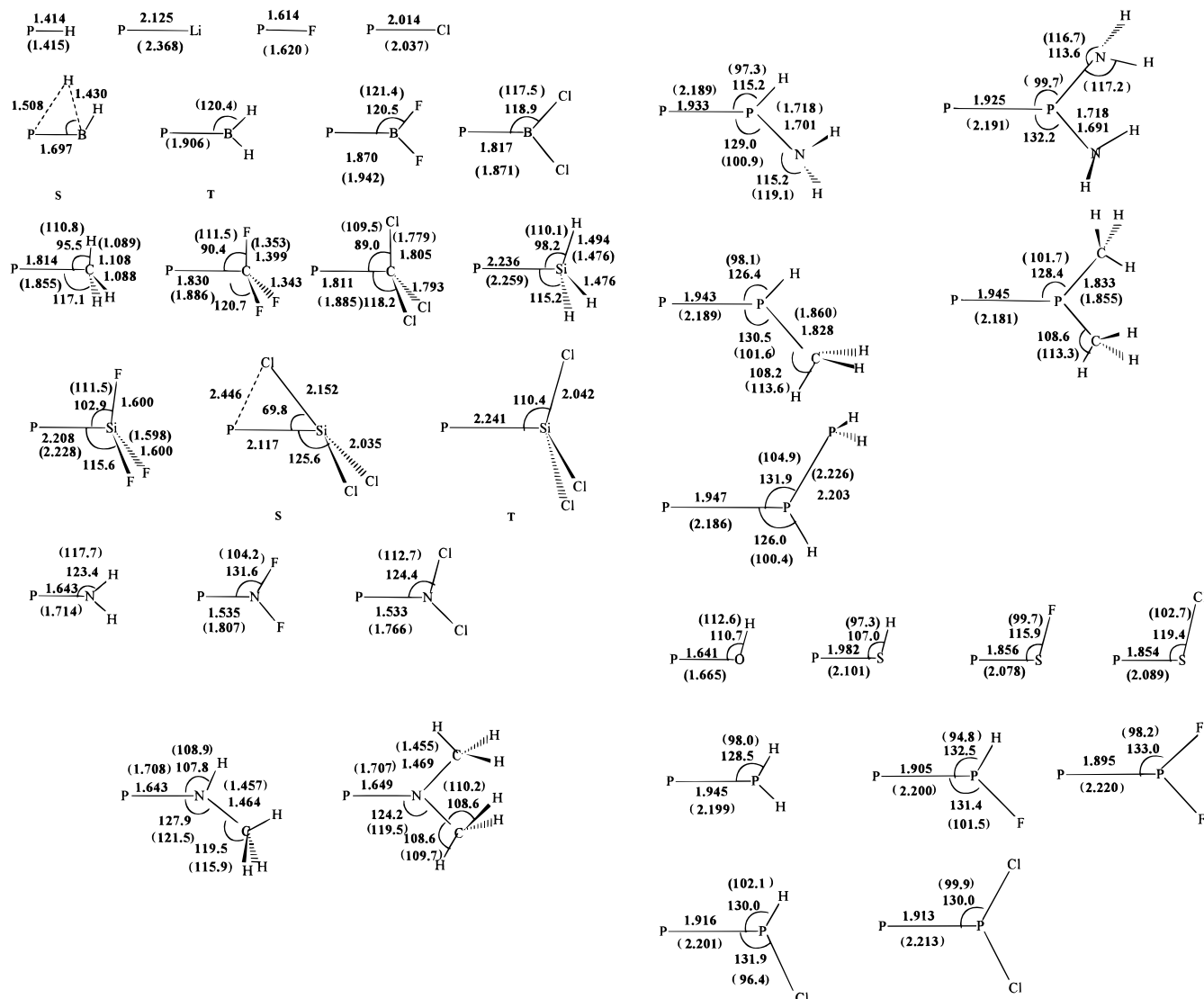


Figure 1. Geometrical parameters for singlet and triplet (in parentheses) substituted phosphinidenes at the (U)MP2/6-31G(d,p) level. Bond lengths are given in angstroms and bond angles in degrees. S and T stand for singlet and triplet states, respectively. The triplet amino- and phosphinophosphinidenes have pyramidal geometries.

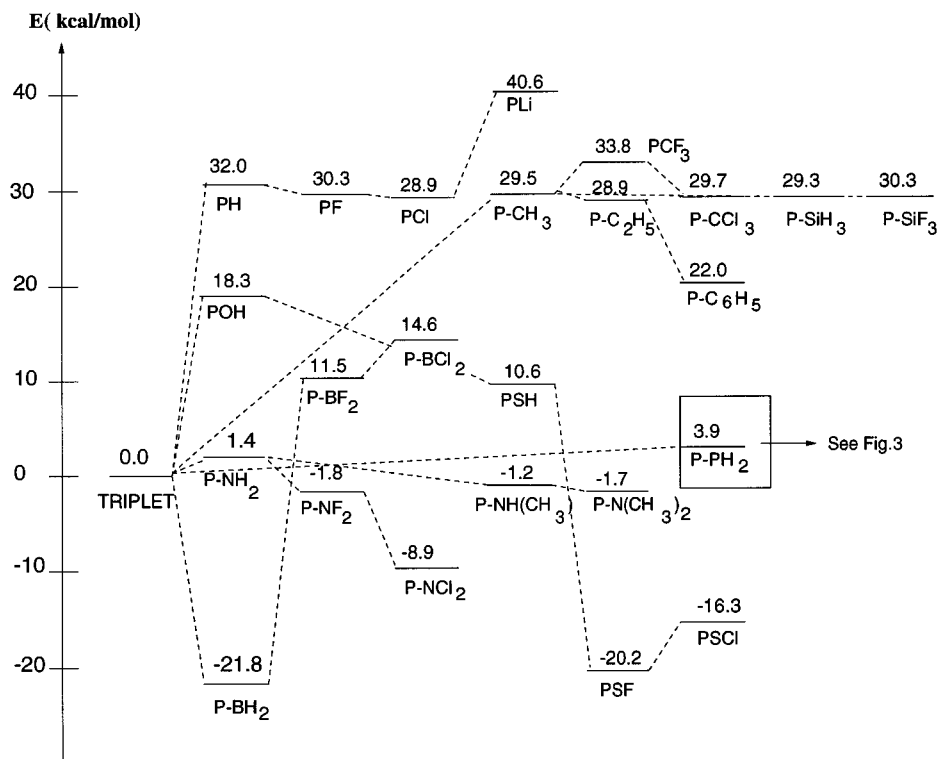


Figure 2. Correlation diagram for the $\Delta E(T-S)$ energy gaps at the QCISD(T)/6-311G(d,p) + ZPE level.

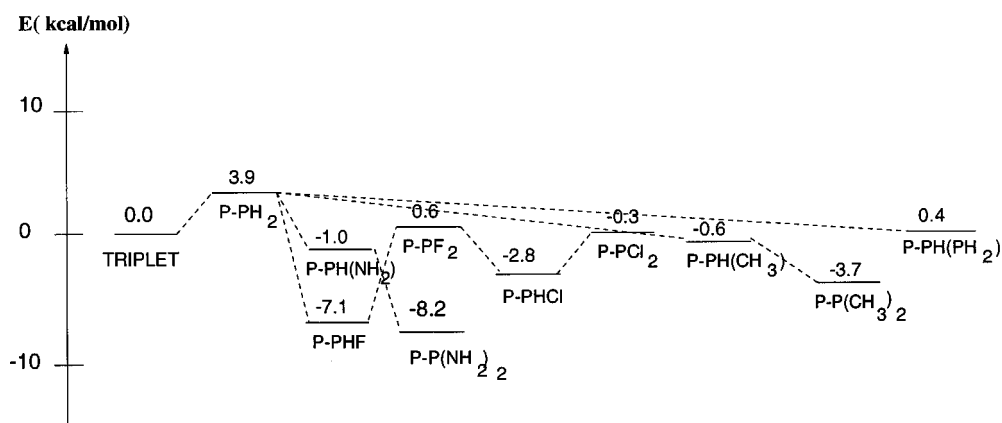


Figure 3. Correlation diagram for the $\Delta E(T-S)$ energy gap in phosphinophosphinidenes ($P-PR_2$) at the QCISD(T)/6-311G(d,p) level.

is the ground state and positive when the singlet is the ground state.

3.1. Diatomic Phosphinidenes. In the four diatomic species considered, the triplet state $^3\Sigma^-$, with a $(\sigma^2\pi_+(\alpha)\pi_-(\alpha))$ electronic configuration, is consistently found to be the ground state. It is worthwhile to mention again that the singlet closed-shell electronic state $^1\Sigma^+$ (π^4)^{30,31} is not the first excited state. In PH, PF, and PCl, the $^1\Delta$ state ($\sigma^2\pi_+(\alpha)\pi_+(\beta)$) is the lowest-lying singlet state, whereas in PLi, the triplet $^3\Pi$ state, having a $(\pi^3\sigma^1)$ electronic configuration, lies lower in energy than the $^1\Sigma^+$ state.³¹

As can be seen in Table 1, the QCISD(T) values for the $\Delta E(T-S)$ are systematically smaller than the CISD(Q) values for the triplet ground state molecules. Extension of the basis set and improvement of correlation treatment tend to reduce the gaps; it is undoubtedly due

to a better description of the singlet $^1\Sigma^+$ states. The $^3\Sigma^- - ^1\Sigma^+$ energy gap in PH is now calculated to be -28 kcal/mol, which is much smaller than the previous value obtained by (U)MP4/6-311++G(d,p) calculations.³⁰ Substitution of H by the electronegative element F does not change the $\Delta E(T-S)$ energy gap. Replacement of H by the second-row Cl atom reduces the gap by only 2.5 kcal/mol. Concerning the electropositive Li atom, our QCISD(T)/6-311++G(3df,2p) value of -42.3 kcal/mol is in good agreement with that of -43.5 kcal/mol reported in ref 31, which used the same method but with the smaller 6-311+G(2df) basis. Note that PNa also has an energy gap similar to that of PLi.³¹ Electropositive elements are known to stabilize the triplet state and hence to increase the $^3\Sigma^- - ^1\Sigma^+$ energy gap.

In summary, diatomic phosphinidenes exhibit a triplet $^3\Sigma^-$ ground state. The $^3\Sigma^- - ^1\Sigma^+$ energy gap is, on the one hand, not significantly affected upon halogen substitu-

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Table 3. Singlet–Triplet Energy Separation in CH₃P Calculated Using Different MO Methods

method	geometry	$E(^3A_2)$ (in hartrees)	$\Delta E(^3A_2 - ^1A')^a$ (in kcal/mol)
MP2(F)/6-31G(d,p)	MP2/6-31G(d,p)	-380.546 66	-35.7
CISD(Q)/6-311G(d,p)	MP2/6-31G(d,p)	-380.603 23	-32.4
QCISD/6-311G(d,p)	MP2/6-31G(d,p)	-380.601 08	-30.8
QCISD(T)/6-311G(d,p)	MP2/6-31G(d,p)	-380.608 59	-29.5
QCISD/6-311++G(d,p)	MP2/6-31G(d,p)	-380.603 61	-31.1
QCISD(T)/6-311++G(d,p)	MP2/6-31G(d,p)	-380.611 21	-29.6
QCISD/6-311++G(3df,2p)	MP2/6-31G(d,p)	-380.656 70	-27.6
QCISD(T)/6-311++G(3df,2p)	MP2/6-31G(d,p)	-380.668 71	-26.0
CCSD/6-311++G(3df/3pd)	CCSD(T)/6-31G(d,p)	-380.660 71	-27.9
CCSD(T)/6-311++G(3df,3pd)	CCSD(T)/6-31G(d,p)	-380.673 24	-26.0
CASPT2(6,9)/ANO ^b	CCSD(T)/6-31G(d,p)	-380.615 95	-25.9
CASPT2(6,13)/ANO ^b	CCSD(T)/6-31G(d,p)	-380.620 16	-25.5
CASPT2(10,12)/ANO ^b	CCSD(T)/6-31G(d,p)	-380.618 63	-25.7

^a Energy difference between the triplet 3A_2 and singlet $^1A'$ states including the zero-point corrections. ^b Atomic natural orbitals having a triplet- ζ plus polarization quality.

tion, but it is, on the other hand, much more influenced by electropositive elements.

3.2. Substituents without Lone Pairs. Boryl Groups. (a) PBH₂. Boryl substitution drastically changes the electronic structure in such a way that the corresponding singlet is more stable than the lowest-lying triplet state, which has a C_{2v} symmetry (3A_2) (Figure 1). Although the corresponding C_{2v} singlet state (1A_1) is not a local minimum on the potential energy surface, but rather a transition structure for hydrogen interchange,^{32,33} it lies about 4.4 kcal/mol below the triplet 3A_2 (QCISD(T)/6-311++G(3df,2p) values). This result is also at variance with that reported in ref 33, where MP4/6-31G(d,p) calculations suggested that the 3A_2 state is 2.8 kcal/mol more stable than the 1A_1 state. The equilibrium singlet PBH₂ exhibits a bridged structure with a PHB two-electron three-center. Given the short P–B distance of 1.697 Å in the singlet PBH₂, as compared with that of 1.832 Å in phosphanylideneborates,³⁴ it is obvious that delocalization takes place from phosphorus electrons into the boron empty p-orbital. Our best estimate places the bridged PHBH singlet 23 kcal/mol below the PBH₂ triplet.

(b) PBF₂ and PBCl₂. Halogenation of the boryl group results in a reestablishment of the triplet ground state (Table 2). In both cases, the C_{2v} singlet structures turn out to be more stable than the bridged forms. Halogen atoms are not well accommodated by bridged structures due to electron repulsion. The empty boron p-orbital is mainly stabilized through π -delocalization of the halogens; therefore, the P lone pairs can no longer delocalize into it. As a result, the singlet state is not stabilized enough to reverse the energy ordering in both PBF₂ and PBCl₂.

Methyl Derivatives. (a) PCH₃. This species has been examined in detail in previous papers.^{35,36} The triplet 3A_2 state is the ground state. The lowest-lying closed-shell singlet state adopts a C_s symmetry ($^1A'$) due to a Jahn–Teller distortion from a C_{3v} structure, which slightly lowers its energy. To test further the effects of basis set and electron correlation on $\Delta E(T-S)$, we have

considered different wave functions for PCH₃. The calculated results are summarized in Table 3. The geometries of both $^1A'$ and 3A_2 were reoptimized using coupled-cluster theory, CCSD(T)/6-31G(d,p), and the single-point energy calculations were performed with this method using a larger basis set, namely the 6-311++G(3df,3pd). On the other hand, the CASPT2/ANO calculations using different active spaces were also performed to emphasize the effect of a multiconfigurational description. It is clear that the QCISD(T), CCSD(T), and CASPT2 results are very close to each other. A consistent value of -26 kcal/mol emerges for $\Delta E(T-S)$ in PCH₃. Relative to PH, a methyl group thus induces a small decrease of only 2 kcal/mol on the energy gap (Table 1). Recently, we have shown that, in carbon-substituted phosphinidenes,³⁷ the smaller singlet–triplet energy seems to arise from a destabilization of the triplet state rather than from a stabilization of the singlet. A similar view has also been put forward³⁸ for the effect of methyl substitution in carbenes.

(b) PCF₃ and PCCl₃. Fluorine and chlorine exert different effects on both geometrical and energetic aspects:

(i) For the singlet state, the Jahn–Teller effect becomes more pronounced, with a larger bending of the PCX bond angles. Only the C–P distance in PCF₃ is slightly stretched relative to that in PCH₃.

(ii) For the triplet state, the C–P bond is stretched in a consistent way in both halogenated species. Regarding $\Delta E(T-S)$, it appears that the CF₃ group slightly enlarges it (4 kcal/mol), whereas the CCl₃ marginally reduces it (0.2 kcal/mol). It seems that, in PCF₃, the triplet state is somewhat stabilized relative to its singlet counterparts. The SOMO–LUMO energy gap in the PCF₃ triplet structure is about 0.7 eV larger than that in PCH₃. CF₃ acts as a σ -electron acceptor group, and thus a negative hyperconjugation from P($n\alpha$)-electrons into $\sigma^*(CF)$ -orbitals could take place. Due to the presence of electrons in both p(P)-orbitals, the triplet state could be more sensitive to this effect than the singlet.

(c) PC₂H₅ and PC₆H₅. The influence of a larger alkyl substituent, i.e., ethyl, has also been examined. Relative to PCH₃, $\Delta E(T-S)$ in PC₂H₅ is reduced by 0.6 kcal/mol (QCISD(T)/6-311G(d,p) values). Nevertheless, it has been recently shown that the singlet ethylphosphinidene

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is not a local minimum on the potential energy surface.³⁹ Upon small distortions from the C_s symmetry, the supermolecule undergoes a barrier-free rearrangement, giving $\text{CH}_3\text{CH}=\text{PH}$. We have also found that, similar to the PCH_3 case, the triplet PC_2H_5 is a stable species lying in deep potential wells.

The phenylphosphinidene, PC_6H_5 , has been the subject of two recent theoretical studies,^{37,40} which pointed toward a triplet ground state (3A_2) and a $^3A_2-^1A_1$ energy gap of -22 ± 3 kcal/mol. The calculated molecular properties of PC_6H_5 are comparable to those of PCH_3 . The isotropic hyperfine splitting constant has been calculated to be $a(^{31}\text{P}) = 66 \pm 3$ G.³⁷ Analysis of some isodesmic reactions suggested again that, relative to methyl, phenyl has a small effect on the energy of the singlet state but appears to destabilize the triplet state and thereby to reduce the $\Delta E(\text{T}-\text{S})$ value.

In summary, carbon-substituted phosphinidenes exhibit a triplet ground state in which the singlet-triplet energy gap is not markedly affected by substituents.

Silyl Derivatives. PSiH_3 , PSiF_3 , and PSiCl_3 . Silylphosphinidenes have a triplet (3A_2) ground state. As far as the calculated results are concerned, silyl substitution also follows the trend discussed above in alkyl substitution: the higher the level of theory, the smaller the $\Delta E(\text{T}-\text{S})$. The electropositive silyl group favors the triplet state by 25.6 kcal/mol, a value comparable to that of methyl. The perhalogenated silyl groups follow a pattern similar to that of methyl derivatives: while the fluorinated group (SiF_3) marginally increases $\Delta E(\text{T}-\text{S})$, the chlorinated group (SiCl_3) slightly reduces it by 4 kcal/mol (at the CISD(Q)/6-311G(d,p) level). Silyl groups are known to favor the triplet state over the corresponding singlet. Even in silylenes (R_2Si), where the singlet state is dominating, silyl substituents can reverse the energy ordering, giving a triplet ground state.⁴¹ In this case, the triplet stabilization apparently comes from a negative hyperconjugation effect, which can roughly be described by the $n(\text{P}) \rightarrow \sigma^*(\text{SiX})$ interaction.

A remarkable structural feature concerns the singlet PSiCl_3 . While the Jahn-Teller distortion in singlet PSiF_3 is even less pronounced than that in singlet PSiH_3 , the chlorinated species actually adopts a bridged P-Cl-Si form. Such a geometrical change is certainly far beyond the magnitude of a Jahn-Teller effect; it arises presumably from the higher tendency of second-row elements to have nonclassical bridged structures. Separate calculations show that the perfluorosilylphosphinidene is a remarkably stable species. In fact, it is found to be -21.5 kcal/mol below its classical isomer $\text{F}_2\text{Si}=\text{PF}$ (value at QCISD(T)/6-311G(d,p) + ZPE).

Comparisons. In going horizontally across row 1 from B to C, although both elements exhibit different properties, they both favor the triplet phosphinidene. The P-BH₂ is an exception due to the formation of a bridged singlet structure; the triplet state is by far more stable in P-BF₂ and P-BCl₂. For its part, methyl substitution destabilizes the triplet state relative to PH and thereby reduces $\Delta E(\text{T}-\text{S})$ by about 2 kcal/mol. The overall electronic effect of a larger alkyl group is a further destabilization of the triplet by, at most, 1 kcal/mol per

CH₂ unit. Phenyl substitution also influences the singlet-triplet gap through an enlarging triplet destabilization. Halogenation of methyl has diverse effects. Fluorination enlarges the gap, whereas chlorination reduces it, but for different reasons. The higher stability of triplet PCX_3 is likely to originate from a negative hyperconjugation.

Substituting C by the second-row analogue PSiX_3 does not significantly modify the pattern, even though the more electropositive silicon atom inherently favors the triplet state. PSiF_3 is a special phosphinidene, as it is more stable than $\text{F}_2\text{Si}=\text{PF}$ and represents thus the global minimum on the F_3SiP potential energy surface.

3.3. Substituents with Lone Pairs. Amino-Substituted Phosphinidenes. (a) P-NH₂. The NH₂ π -donor group enormously stabilizes the singlet state; $\Delta E(\text{T}-\text{S})$ is strongly reduced to only -1.2 kcal/mol at our most sophisticated level. In view of this small value, it cannot be ruled out that the singlet could become the ground state at even higher levels of theory. It is reasonable to assume that both singlet and triplet states in P-NH₂ are quasi-degenerate. Interaction of the nitrogen lone pair with the empty p(P)-orbital is the origin of the high singlet stabilization. Geometrical features already give some important information concerning the electronic structure and bonding in the singlet aminophosphinidene. As a matter of fact, the planar singlet form suggests a good realization of the delocalization mentioned above. The different P-N distances can be compared as follows: singlet P-NH₂, 1.643 Å, triplet P-NH₂, 1.714 Å; P-N in $\text{H}_2\text{P}-\text{NH}_2$, 1.68 Å; and the experimental value of 1.544 Å in $\text{Me}_3\text{Si}(t\text{Bu})\text{-NP}=\text{N}^t\text{Bu}$.⁴² Thus, the singlet P-N bond has a more-than-single-bond character.

(b) P-NF₂ and P-NCl₂. Substitution of hydrogen in NH₂ by halogens favors the singlet, making it now the ground state.¹⁶ However, the $\Delta E(\text{T}-\text{S})$ values remain small and are not larger than 9 kcal/mol. This additional singlet energy gain apparently originates from a back-donation exerted by halogen atoms into the p(π^*)-orbital of both N and P atoms. Again, the singlet state exhibits some geometrical changes, in particular the P-N bond shortening, which becomes even more pronounced, i.e., 1.535 Å in PNF_2 and 1.533 Å in PNCl_2 . Note that the experimental distance in the PN molecule amounts to 1.491 Å.

(c) P-NH(CH₃) and P-N(CH₃)₂. As amino substitution favors the singlet structure, it is of interest to examine the behavior of stronger electron donor groups. At the QCISD(T)/6-311G(d,p) level, the singlets P-NH(CH₃) and P-N(CH₃)₂ lie 1.2 and 1.7 kcal/mol below their corresponding triplets. Relative to PNH_2 , these energy gaps represent stabilization of 2.8 and 3.1 kcal/mol, respectively. The effect of methyl groups is not really additive; it is dominated by the first group. Geometrical parameters are also in line with energetic results. The singlet structures are always planar, with shortened P-N bond lengths, i.e., 1.643 Å in P-NH(CH₃) and 1.649 Å in P-N(CH₃)₂, indicative of a π -donating effect of the entire amino substituent.

The second factor influencing $\Delta E(\text{T}-\text{S})$ is the steric nuclear repulsion in the triplet state. This is illustrated by the fact that triplet phosphinidene is distorted from the pyramidal geometry in taking a conformation closer to the planar structure; the CNPC dihedral angle is 149°.

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A planar triplet phosphinidene is, of course, much less stable than a pyramidal counterpart, due to the electron repulsion between $p(\alpha)(P)$ - and $p(\pi)(N)$ -electrons. As mentioned in the Introduction, decomposition of an aminophosphirane is best proceeded through a low-lying singlet state of an aminophosphinidene. Our theoretical results lend support for this view and suggest, in addition, that the aminophosphinidene generated in these reactions is likely to have a singlet ground state.

Phosphino-Substituted Phosphinidenes. (a) P-PH₂, P-PHF, P-PF₂, P-PHCl, and P-PCl₂. These species have been examined in previous papers.^{43,44} We supplement here some results obtained using higher level calculations. In general, the behavior of phosphino groups is similar to that of amino groups. Their π -donor properties are thus expressed in the largely reduced $\Delta E(T-S)$ values. This is again manifested in the singlet geometries, which differ clearly from the triplets. The singlet P-P bond of 1.945 Å in P-PH₂ is even shorter than the double bond in $\phi P=P\phi$ (2.034 Å), while the corresponding triplet bond has a length of 2.199 Å.

As pointed out in a previous paper,⁴⁴ monofluorination reverses the electronic state ordering, making the singlet the ground state. Nevertheless, $\Delta E(T-S)$ in PPHF is still small (7.1 kcal/mol).

Unexpectedly, perfluorination lowers the triplet, which again becomes the ground state, lying 0.6 kcal/mol under the singlet. Upon monochlorination of the phosphino group, $\Delta E(T-S)$ is about 2.8 kcal/mol in favor of the singlet state. Upon perchlorination and compared to P-PH₂, the singlet ground state is reinforced, lying now 0.3 kcal/mol below the triplet. A general observation is that perhalogenation stabilizes the triplet state, while monohalogenation destabilizes it in such a way that an energy ordering reversal effectively occurs in P-PHF and P-PHCl. A possible reason for this phenomenon is a geminal interaction of both halogen atoms in the triplet state, which may enhance its stabilization through negative hyperconjugation. It can be concluded that both PPF₂ and PCl₂ species feature quasi-degenerate triplet and singlet states, whereas in both PPHF and PPHCl, the singlet state is slightly favored.

(b) P-PH(CH₃), P-P(CH₃)₂, P-PH(NH₂), P-P(NH₂)₂, and P-PH(PH₂). We have seen that the π -electron-donating effect of PH₂ is less effective than that of NH₂. A question of interest concerns the groups that enhance the π -donor capacity of the phosphino substituent. As can be seen in Table 2, a methyl substituent further lowers the singlet state by placing it less than 1 kcal/mol below the triplet state. Again, both states are presumably quasi-degenerate. A second methyl group significantly enlarges $\Delta E(T-S)$ by 3.7 kcal/mol in favor of the singlet. Apparently, methylation of a phosphino group implies a behavior comparable to that of the methylated amino group.

We now investigate whether the amino moiety influences the electronic state by means of lone pair repulsion. At our most sophisticated level, we find a singlet ground state for P-PH(NH₂), with a $\Delta E(T-S)$ of 1.0 kcal/mol. Compared to P-PH₂, the singlet state is slightly stabilized by 5 kcal/mol. An eventual triplet destabilization is reflected in the pyramidal character of P, the dihedral

angle being 96.2° in PPH₂ but 116° in PPH(NH₂). Double amino substitution enlarges $\Delta E(T-S)$ to 8.2 kcal/mol. Again, the larger $\Delta E(T-S)$ separation can in part be attributed to a repulsion between lone pairs of both amino groups and the phosphino lone pair, which disfavors the triplet.

The P-PH(PH₂) molecule is constituted of only P atoms. The triplet state lies 0.4 kcal/mol under the singlet. The calculated gap is too small to be unambiguous. On the one hand, compared to the -PH(NH₂) group, the -PH(PH₂) substituent is somewhat weaker in its π -donor capacities, even though delocalization takes place over p-orbitals of the same type and size. On the other hand, when comparing this result with that for P-PH₂, the additional phosphino group in the β -position lowers the singlet state by 3.5 kcal/mol. Separate calculations show that both -P(NH₂)₂ and -P(PH₂)₂ groups also favors the singlet state, but the effect is not additive.

Hydroxyl and Thiohydroxyl Groups. Both POH and PSH have triplet ground states lying 16.9 and 6.1 kcal/mol, respectively, under the singlets. The OH and SH substituents act as π -electron donors with smaller donating capacity than that of NH₂ or PH₂, because of the sp³ hybridization state of the oxygen and sulfur lone pairs.

Triplet and singlet POF species do not exist as local minima. Any attempt to optimize either the singlet or the triplet state resulted in the radical fragments PO• + F•. This dissociation is a consequence of the repulsion between nonbonding electrons on both fluorine and oxygen atoms. Although both electronic states of POCl have been located ($\Delta E(T-S) = +7$ kcal/mol), these species are highly unstable. This is reflected in the large energy difference of 68.3 kcal/mol between ground state POCl and its isomer ClP=O.⁴⁷ The thiohydroxyphosphinidene (PSH) was recently generated from its cation in an experiment using neutralization-reionization mass spectrometry.¹⁸ As expected, no information on the electronic state of the observed species could be gathered. Our best estimate places the singlet PSH 6.1 kcal/mol above its triplet ground state, in agreement with an earlier study.⁴⁵ Substituting oxygen by its second-row sulfur analogue lowers the singlet energy by about 10.8 kcal/mol. Considering the P-S bond lengths in the singlet state (1.982 Å) and triplet state (2.101 Å), and a double P-S bond in the PCH₂S₂⁻ anion (1.978 Å),⁴⁶ it can be seen that the singlet P-S bond has dative π -bond character. Since the p-orbitals of the P atom resemble more in size those of S than those of O, a better overlap between P- and S-orbitals results in a relatively larger singlet stabilization for PSH. The kinetic stability of singlet PSH is also checked by the energy barrier for unimolecular rearrangement. This barrier amounts to 23 kcal/mol, while the HP=S isomer lies 25 kcal/mol under singlet PSH. Similarly, the singlet POH is also stable with respect to 1,2-H shift; the corresponding barrier is calculated to be 30 kcal/mol, whereas the HP=O isomer is 35 kcal/mol more stable than POH.

Contrary to POF, halogenation of the thiohydroxyl group is successful in such a way that the singlet state becomes the ground state by larger $\Delta E(T-S)$ values of

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20.2 kcal/mol in PSF and 16.3 kcal/mol in PSCI. The π -back-donation of F, which mainly controls the singlet lowering, is thus more effective, as demonstrated in the very short P–S bond length of 1.856 Å. Although the singlet PSF differs by a large energy amount from its triplet, it is not stable toward unimolecular rearrangement. The transition structure for 1,2-F shift giving FPS lies only 4.6 kcal/mol above PSF in its singlet state. In contrast, the energy barrier for 1,2-Cl shift is larger, 28.8 kcal/mol relative to PSCI.

In summary, the dominant factor in stabilizing the singlet state is, without exception, the attachment of substituents with π -type lone pairs to the phosphinidene moiety. Of the first-row elements corresponding to the groups V and VI, group V elements most strongly stabilize the phosphinidene singlet state. In going to the second-row elements, group VI substituents have larger impact on the singlet stabilization.

3.4. General Conclusion. The correlation diagrams displayed in Figures 2 and 3 summarize the $\Delta E(T-S)$ values for all substituted phosphinidenes considered. A number of general conclusions can be drawn:

(1) Single element substitution does not significantly influence the singlet–triplet gap. The triplet $^3\Sigma^-$ is the ground state.

(2) Group III substituents such as the boryl group favor the singlet state by means of π -delocalization of the P lone pair electrons into the boron empty p-orbital. Halogenation of the boryl group, however, diminishes this effect, resulting in a triplet ground state. Borylphosphinidenes are likely to have triplet ground states.

(3) Group IV substituents such as the methyl group hardly reduce the singlet–triplet gap as compared to PH. The induced changes are not larger than 2 kcal/mol. On increasing the alkane chain, the singlet is stabilized by at most 1 kcal/mol per CH_2 unit. Phenyl substitution slightly reduces the gap by destabilizing the triplet state. Fluorination of methyl enlarges the triplet due to a negative hyperconjugation between $\rho\alpha(\text{P}) \rightarrow \sigma^*(\text{CF})$, which lowers the triplet energy. Second-row elements such as the investigated silyl groups also do not significantly affect the situation, changing by no more than 3 kcal/mol $\Delta E(T-S)$ as compared to their methyl analogues. Overall, the triplet state is unambiguously established as the ground state for these categories.

(4) In going to the substituents containing lone pairs, a few factors come into play in making the singlet the electronic ground state. The dominating factor is the classical π -donation from the substituent to the phosphorus empty $3p(\pi)$ -orbital. This electron delocalization

becomes somewhat stronger upon putting methyl and/or amino groups, halogen atoms, or any π -donating entities at the β -position. The larger the π -donation, the more stabilized the singlet state. Nevertheless, the $\Delta E(T-S)$ values are relatively small in most cases, amounting to less than 10 kcal/mol. The lowest lying singlet ground states are found for PSF (a gap of 20 kcal/mol) and PSCI (a gap of 16 kcal/mol). With regard to amino and phosphino groups, the size of β -substituents also plays an important role. The bulkier the β -groups, the stronger the nuclear repulsion, the less pyramidal the triplet geometry becomes, and the more destabilized the triplet state could be.

The following chart, in which each group is split into first and second rows and compared with its neighbor group, summarizes our findings:

group row	III	IV	V	VI	Halogens
1	T	T	S, T	S	T
2		T	S, T	S	T

In this context, the groups, which are practical for an experimental preparation, are the amino and phosphino substituents. Phosphinidenes having a singlet ground state are expected to be effectively formed by using one of these two groups and enlarging the size of their β -substituents, for example, by using bulkier alkyl groups. The latter contribute, on the one hand, to stabilize the singlet state by an electronic effect and, on the other hand, to destabilize the triplet state by a steric effect.

The $\text{P-P}(\text{Bu})_2$ species generated by Fritz and co-workers¹⁴ is likely to have a singlet ground state unambiguously lying well below its triplet counterpart. Several less stable aminophosphinidenes (P-NR_2) trapped in metal complexes³ are also expected to have a singlet ground state. In a future study, we will examine the influence of substituents at both α - and β -positions on the electronic structure of phosphinidenes.

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