

Electronic Structure of λ^5 -Phosphaacetylenes and Corresponding Triplet Methylene

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Abstract: The electronic structure and geometry of H_2PCSiH_3 (**1**) and $(\text{NH}_2)_2\text{PCSiH}_3$ (**3**) were investigated by extended basis set (DZP) ab initio molecular orbital theory. Both singlet and triplet structures for **1** and **3** are considered. The calculated structure for **1** (ground state) is best characterized as a P-C multiply bonded species with an extremely short (159.5 pm) bond. The phosphorus center is planar in the ground state, and the P-C-Si angle is 137.9° . Contrary to expectations based on a singlet carbene model for the ground state, the P-C bond lengthens upon protonation of the carbon center. The lowest triplet state of **1** is only 5.6 kcal/mol above the ground-state structure. The structure of the triplet is remarkably different from that of the ground state, with a P-C bond length of 180.0 pm and a pyramidal phosphorus center. The P-C-Si angle remains large (144.1°), and the triplet state is best characterized as a triplet methylene. Replacement of the two hydrogens on phosphorus in **1** by two NH_2 groups to form **3** has little effect on the geometry of the triplet but has a pronounced effect on the singlet. The P-C bond in **3** shortens to 152.5 pm, and the P-C-Si angle becomes almost linear. The singlet-triplet splitting increases by a factor of 2.3 to 13.9 kcal/mol.

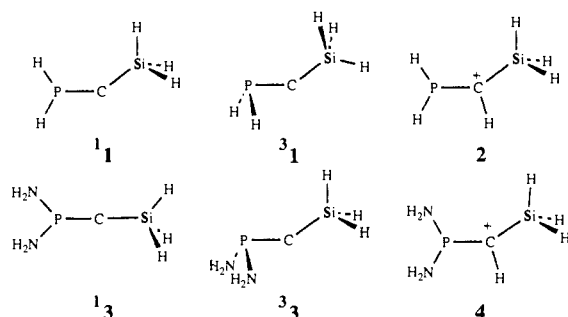
Introduction

The recent isolation and characterization of two structures which can be formulated as carbenes (or methylenes)^{1,2} has prompted considerable discussion about the true nature and best description of the ground states for these molecules.³ A 2-coordinate carbon has the potential for carbene (singlet) or methylene (triplet) character⁴ if the valence at the carbon is genuinely two (i.e. a 6-C-2 center⁵). Problems can arise in determining the valence of the carbon if the ligand atoms are capable of non-traditional bonding. If the ligating atoms belong to the first or second period (H-Ne), the problem is usually simple. When the 6-C-2 arrangement (valency 2) is evident after the octets of the ligand atoms have been satisfied, then the species can be considered as a carbene or methylene. As examples, H_2C : is clearly the ground-state triplet methylene and F_2C : is the ground-state singlet difluorocarbene. On the other hand, in the ground state, the central carbon of acetonitrile *N*-oxide ($\text{CH}_3\text{C}\equiv\text{N}^+-\text{O}^-$) is much better described as a triply bonded nitrile carbon than as methyl(nitroso)carbene or methyl(nitroso)methylene ($\text{CH}_3\text{C}-\text{N}=\text{O}$).⁶ If the ligand atoms are from the third period (Na-Ar) or higher ones, there is always the possibility of the ligand having more bonds than expected from the normal Lewis counting rules. This complication has been previously recognized for $\text{F}_3\text{S}\equiv\text{C}-\text{CF}_3$ ⁷ and $\text{R}_2\text{P}\equiv\text{C}-\text{SiR}_3$ ^{1,8} structures. If this type of compound were to have a divalent carbon, then its ground state is likely to be a triplet (methylene) as both of the substituents are electropositive and it is quite well-established that electronegative (π -donor) substituents are required to generate a singlet ground state (carbene).⁹ We have previously addressed these issues in the imidazol-2-ylidene systems.^{2b} With these complications in mind, we have undertaken

a theoretical study of the simplest model system H_2PCSiH_3 (**1**) and of the one where amino groups are substituted for the hydrogens on phosphorus, $(\text{NH}_2)_2\text{PCSiH}_3$ (**3**). The structures considered are **1**, **3**, and the protonated species **2** for H_2PCSiH_3 , and **3**, **3**, and the protonated species **4**.

Calculations

The calculations were done with a polarized, valence double zeta basis set. The carbon and hydrogen basis sets are from Dunning and Hay.¹⁰ The phosphorus and silicon basis sets are from McLean and Chandler¹¹ with respective d orbital exponents of 0.5 and 0.4. The geometries of the singlets (RHF) and triplets (ROHF) were gradient-optimized at the SCF level.¹² The force fields were calculated analytically for the RHF singlets and the ROHF triplets.¹³ These calculations were done with the program



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Table I. Molecular Geometries^{a,b}

property	¹ 1	¹ 1 (MP-2)	³ 1	³ 1 (UMP-2)	2	¹ 3	³ 3	4
r(P-C)	159.5	160.0	180.0	177.4	162.7	152.5	180.2	160.1
r(Si-C)	184.4	184.3	185.5	184.2	193.9	180.6	185.2	190.5
r(P-H ₁)	139.5	140.9	140.8	140.8	138.2			
r(P-H ₂)	138.4	138.8	140.9	140.8	138.1			
r(P-N ₁)						166.2	170.0	160.7
r(P-N ₂)						166.1	170.1	160.9
r(Si-H ₃)	148.4	148.2	147.9	147.5	146.7	148.4	147.7	147.2
r(Si-H ₄)	147.5	147.4	147.6	147.1	146.2	148.1	147.7	146.6
r(Si-H ₅)	147.6	147.4	147.9	147.5	146.3	148.1	147.7	146.6
r(N ₁ -H ₇)						99.7	100.0	100.0
r(N ₁ -H ₈)						99.8	99.9	100.1
r(N ₂ -H ₉)						99.8	99.6	100.1
r(N ₂ -H ₁₀)						99.7	99.8	100.0
r(C-H ₆)					108.0			107.9
θ (P-C-Si)	137.9	131.2	144.1	148.7	126.3	175.9	145.9	128.4
θ (H ₁ -P-C)	129.9	133.8	99.1	98.8	120.6			
θ (H ₂ -P-C)	122.5	121.8	98.9	98.8	122.7			
θ (H ₁ -P-H ₂)	107.5	104.4	95.5	95.2	116.6			
θ (N ₁ -P-C)						131.2	98.3	125.7
θ (N ₂ -P-C)						129.9	101.2	125.9
θ (N ₁ -P-N ₂)						99.0	106.6	108.4
θ (H ₃ -Si-C)	115.7	116.5	110.4	110.4	105.3	113.9	110.5	106.4
θ (H ₄ -Si-C)	108.2	108.0	108.8	109.0	105.0	110.9	110.3	107.9
θ (H ₅ -Si-C)	107.5	108.0	110.5	110.4	104.6	110.5	109.5	107.3
θ (H ₆ -C-P)					115.6			113.6
θ (H ₆ -C-Si)					118.2			118.0
θ (H ₇ -N ₁ -P)						115.6	119.1	121.4
θ (H ₈ -N ₁ -P)						118.5	114.9	121.5
θ (H ₇ -N ₁ -H ₈)						113.6	111.0	115.7
θ (H ₉ -N ₂ -P)						118.3	116.4	121.7
θ (H ₁₀ -N ₂ -P)						115.3	121.3	121.1
θ (H ₉ -N ₂ -H ₁₀)						113.6	112.5	115.7

^a Bond distances in picometers and angles in degrees. ^b Hydrogens are numbered as in Figure 1, with N₁ bearing H₇ and H₈.

Table II. Calculated Energies

level	total energies (au)							
	¹ 1	³ 1	³ 1 (projected)	2	¹ 3	³ 3	³ 3 (projected)	4
SCF	-670.298 416	-670.324 630		-670.694 383	-780.463 125	-780.448 147		-780.856 543
UHF		-670.332 903	-670.337 215			-780.456 243	-780.460 443	
MP-2	-670.646 454	-670.632 606	-670.635 544	-671.042 085	-781.121 654	-781.089 399	-781.092 235	-781.536 912
MP-4(SDTQ)	-670.704 888	-670.694 144	-670.695 973	-671.102 045	-781.193 827	-781.169 931	-781.171 747	-781.612 140
MP-2/MP-2	-670.647 267	-670.632 861	-670.635 887					
MP-4/MP-2	-670.705 876	-670.694 295	-670.696 188					
Singlet - Triplet Energy Difference (kcal/mol)								
level	¹ 1 - ³ 1 ^{a,b}	¹ 3 - ³ 3 ^a		level	¹ 1 - ³ 1 ^{a,b}	¹ 3 - ³ 3 ^a		
MP-2	8.7 (9.0)	20.2		MP-4	6.7 (7.3)	15.0		
PMP-2	6.8 (7.1)	18.5		PMP-4	5.6 (6.1)	13.9		

^a ΔE between SCF and ROHF geometries. ^b Numbers in parentheses are ΔE between MP-2 and UMP-2 geometries.

GRADSCF¹⁴ as implemented on a Cray YMP computer system. Subsequent calculations at the correlated level were performed as follows. Perturbation theory calculations¹⁵ through the RHF/MP-4(SDTQ) level for the singlets and through the UHF/MP-4(SDTQ) and UHF/PMP-4(SDTQ) levels for the triplets were done with the same basis set at the optimum SCF geometries. These calculations included only the valence electrons. The notation PMPx means projected MP. This level corresponds to projecting out the higher level spin contaminants to the UHF wavefunction. The spin projection is done following the formalism of Schlegel.^{15c} The PUMP-4(SDTQ) level corresponds to the MP-4(SDTQ) calculation based on the UHF wavefunction, with the spin projection correction approximated as that from the PUMP-3 level. For comparison, the geometries of ¹1 and ³1 were

also optimized at the MP-2 level. The perturbation theory calculations were done with the program GAUSSIAN-90¹⁶ as implemented on a Cray YMP computer.

Results and Discussion

The results for the geometries are shown in Table I and the total energies are given in Table II. The optimized geometries for ¹1, ³1, **2**, ¹3, ³3, and **4** are depicted by the KANVAS¹⁷ drawings in Figure 1. There is a clear difference in the structures of the singlet (¹1) and the triplet (³1). The singlet (¹1) has a planar PH₂ group and a very short P-C bond (159.5 pm). The P-C-Si bond

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(17) These drawings were made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

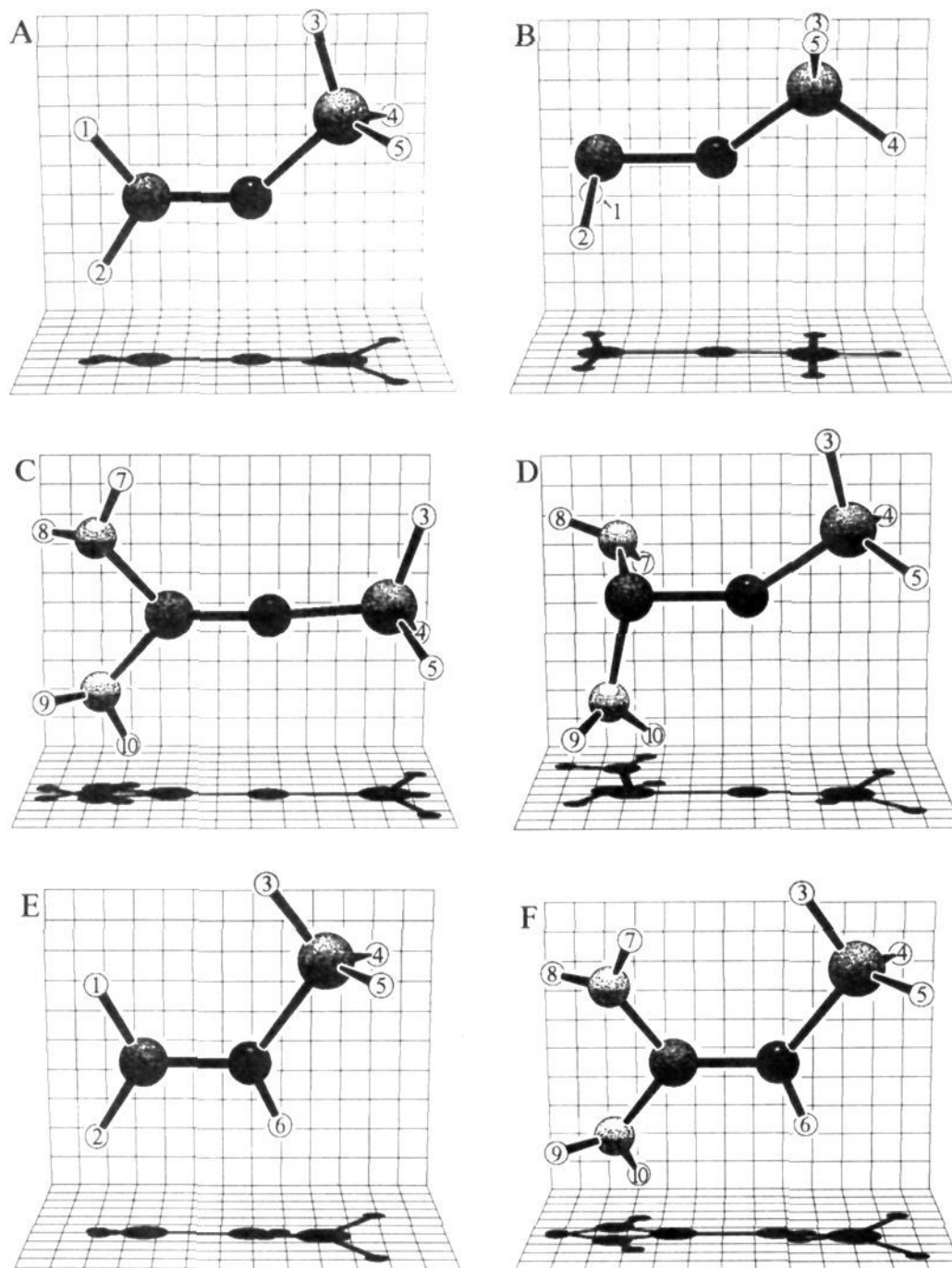


Figure 1. KANVAS¹⁷ drawings of (A) ¹I; (B) ³I; (C) ¹3; (D) ³3; (E) 2; and (F) 4.

angle is opened up to 138°. For comparison, bond angles at carbon in singlet carbenes are small (e.g. in singlet CH₂,¹⁸ $\theta_{(\text{HCH})} = 102.8$ and in CF₂,¹⁸ $\theta_{(\text{FCF})} = 104.7$). The SiH₃ group is a typical tetrahedral silicon with a slightly shortened C-Si bond ($r_{(\text{Si-C})} = 186.9$ pm in CH₃SiH₃).¹⁹ The triplet (³I) has an even larger bond angle at carbon of 144°, with a long P-C bond of 180.0 pm and a pyramidal PH₂ group like that of PH₃. The bond angle at carbon is even larger than that in simple triplet methylenes (e.g. in CH₂,¹⁸ $\theta_{(\text{HCH})} = 128.8$). The silyl group has been previously reported to give methylenes with large valence angles at carbon.²⁰ There

is very little change in the C-Si bond and the SiH₃ group between ¹I and ³I. The only changes in the structures at the correlated MP-2 level are in the bond angles at carbon. For ¹I, the bond angle decreases by ~7° and for ³I it increases by ~5°.

Replacement of the hydrogens at phosphorus by amino groups leads to significant changes in the structures for the singlet. For ¹3, the P-C bond becomes even shorter (by 7 pm) and the P-C-Si angle becomes almost linear. Thus, this structure is essentially that expected for a λ^3 -phosphaacetylene. Consistent with the near-linear arrangement at carbon, the Si-C bond decreases by 3.8 pm. The phosphorus remains planar, but both amines are slightly pyramidal. The structure of the substituted triplet (³3) is essentially unchanged from that of the unsubstituted structure

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(³1). The P-N bonds lengthen by 4 pm in going from ¹3 to ³3 and the nitrogens remain slightly pyramidal.

At the correlated MP-2 level, ¹1 is lower in energy than ³1 by 8.7 kcal/mol.²¹ This difference decreases to 6.7 kcal/mol at the MP-4(SDTQ) level and to 5.6 kcal/mol at the PMP-4 level. Thus, ³1 is close in energy to ¹1, but at room temperature the equilibrium constant is only 8.8×10^{-5} , so that at equilibrium there will be about 0.01% of the triplet present in solution at 25 °C. The small amount of triplet may not be readily detected by EPR techniques. The triplet could play a kinetic role if it reacted with lower activation energies than the singlet and if access to this triplet state was not blocked by an activation barrier. Considering the very different geometries of ¹1 and ³1, such an activation barrier could be substantial. Use of the correlated MP-2 geometries leads to very small changes in ΔE (¹1 - ³1).²² Substitution of the amino groups to form **3** leads to pronounced changes in the singlet-triplet splitting. The splitting for **3** increases by a factor of ~2.3 to 13.9 kcal/mol at the PUMP-4(SDTQ) level. Thus, there will be no likelihood of observing the triplet at room temperature for the species **3**.

The proton affinity of ¹1 is 243.1 kcal/mol at 300 K, obtained by using an electronic energy difference of 249.2 kcal/mol at the MP-4 level and the appropriate corrections.²⁴ This value is similar to that calculated for the protonation of imidazol-2-ylidene (257.3 kcal/mol).^{2b} However, the structure of ¹1 does not respond to protonation as would be expected for a carbene. We have pre-

viously shown that the structural and electronic relation between a carbene and its corresponding carbenium ion (formed by protonation of the carbene center) provides a useful diagnostic for classifying divalent carbon species.^{2b} Protonation of a singlet carbene center is expected to give a decrease in the carbon-substituent bond lengths and an increase in the characteristically small valence angle between the original substituents at carbon. The P-C bond in **2** is longer than that in ¹1, and the P-C-Si angle decreases rather than increases. Substitution of the amino groups on phosphorus leads to an increased proton affinity for ¹3 (257.0 kcal/mol based on an electronic energy difference of 262.5 kcal/mol at the MP-4(SDTQ) level) over ¹1. As with ¹1, ¹3 similarly does not respond to protonation like a carbene. The P-C bond increases by 7.6 pm in **4** and the Si-C bond increases by 9.9 pm. The bond angle at carbon decreases substantially to 128.4°. The P-N bond distances in **4** decrease by 5.5 and 5.2 pm as compared to those in ¹3. This is consistent with the increase in $r_{(P-C)}$ of 7.6 pm predicted for going from ¹3 to **4**. Thus both cations, **2** and **4**, have fairly similar structures, although both the C-Si and C-P bonds shorten slightly by 3.4 and 2.6 pm, respectively, in **4** as compared to **2**. Both **2** and **4** resemble an experimental structure determination of a C trimethylsilylated analogue of these cations, $[(CH_3)_2N]_2P-C^+-[Si(CH_3)_3]_2$ ($r_{(P-C)} = 162.0$ pm, $r_{av(Si-C)} = 189.4$ pm, $\theta_{av(P-C-Si)} = 120.5^\circ$).²⁵

These data support the best characterization of ground state ¹1 and ¹3 as multiply bonded λ^5 -phosphaacetylenes. There are low-lying triplet methylene states (³1 and ³3) which can best be described as λ^3 -phosphinomethylenes. Large structural differences in singlet and triplet states may give rise to a substantial activation barrier between the two sets of species.

Registry No. **1**, 136202-70-5; **2**, 136202-71-6; **3**, 136202-72-7; **4**, 136202-73-8.

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(21) It is well-known that triplet calculations at the ROHF or UHF levels incorporate some of the effects of the correlation energy, whereas closed-shell SCF calculations do not. Thus, it is inappropriate to take an energy difference from a closed-shell SCF calculation and an open-shell calculation.

(22) The singlet-triplet splitting for **1** is similar to that calculated for PH₂CH of 6.2 kcal/mol at the DZ+P/PMP-4 (SDTQ) level. This calculated value is twice the splitting previously reported for this energy difference at the MP-3 level.²³

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Synthesis, Structure, and Dynamics of a Macrocyclophane

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Abstract: The synthesis of the macrocyclophane **6** by intramolecular alkyne trimerization using Vollhardt's catalyst is presented. The construction is composed of one 1,3,5-substituted benzene and one 2,6,10-triaminotrioxatricornan subunit linked by three tetramethylene arms. The crystal structures of **5**-tos/**6**-tos and **6** have been determined. **5**-tos/**6**-tos shows a structure distorted from a helical C₃ symmetric conformation, and **6** shows a structure of C₁ symmetry with a void in the interior. Empirical force field and semiempirical calculations, and conformational analysis by ¹H NMR techniques, support a noncollapsed solution structure of **6**. Low-temperature ¹H NMR of **6** reveals a dynamic behavior consistent with a stepwise flip of pitch of the tetramethylene chains.

Macrocages with physical properties stemming from intricate molecular connectivities require the synthesis and characterization of multiply bridged macrocyclophanes.¹ These macrocages have a greater stereochemical complexity² than their toroidal coun-

terparts;³ control of their structure and elucidation of their stereochemistry pose a substantial challenge.⁴

Synthesis

Synthesis of triply bridged macrocyclophanes has been accomplished from three general approaches: (1) coupling of two

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