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On the nature of the CP group adjacent to a valence-deficient atom: phosphaehtynyl substituent vs. phosphorus center

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ABSTRACT: On the basis of quantum chemical calculations (CCSD(T), CASSCF and B3LYP), we have demonstrated in this work that the $\text{—C}\equiv\text{P}$ group, when connected to a valence-deficient center, in particular in a triplet state or a radical, its π -electrons tend to move into other parts of the system, thus transforming the formal $\text{RC}\equiv\text{P}$ system into a P-centered RC—P species. The CP group does not behave as a phosphaehtynyl substituent, but rather as a P-centered phosphinidene or a P-radical. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculations; valence-deficient atom; phosphaehtynyl substituent; phosphorus center

INTRODUCTION

The RCP molecules are known to form the phosphalkyne functional group. In a simple member featuring a closed-shell singlet ground state, the CP group is consistently characterized to be a typical carbon–phosphorus triple bond, $\text{—C}\equiv\text{P}$, and R a substituent. Proceeding in the opposite direction, the CP also behaves as a phosphaehtynyl substituent. As such, this substituent exerts a remarkably strong electron donor effect, which tends to enhance the electron density and basicity of the attaching moieties R.

Recently, the HCCP molecule has been detected for the first time using microwave spectroscopic techniques.¹ The latter species can formally be regarded as a carbene, in which a hydrogen atom of methylene is replaced by a CP group. However, the recorded rotational transitions of HCCP and its isotopically substituted congeners, as well as the observed hyperfine splitting constants, appeared to be more consistent with a linear framework and a triplet ground state, in which the phosphalkyne functional group no longer exists.

The derived r_o structure of HCCP suggested a short $r_o(\text{CC}) = 1.241 \text{ \AA}$ and a long distance $r_o(\text{CP}) = 1.685 \text{ \AA}$. In fact, although the latter distance is longer than the

length of a $\text{C}\equiv\text{P}$ triple bond of around 1.54 \AA , the former distance is closer to the typical value of a $\text{C}\equiv\text{C}$ triple bond ($1.21\text{--}1.22 \text{ \AA}$) than that of a $\text{C}=\text{C}$ double bond ($1.33\text{--}1.34 \text{ \AA}$). The spin density of the unpaired electron was also estimated to be largely concentrated on the P atom (76%).¹

Subsequent quantum chemical studies^{2–4} confirmed this view. Calculations using coupled-cluster CCSD(T) and multi-configurational second-order perturbation CASPT2 theories, as well as density functional theory with B3LYP functional calculations on the halogenated XCCP series, with $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$ and I , pointed out that each XCCP molecule has a linear triplet ground state.⁴ In this high-spin state, the molecule can best be regarded as a phosphinidene derivative, $\text{X—C}\equiv\text{C—P}^\bullet$.

The singlet phosphinidene counterparts have been shown to have an open-shell electronic configuration and also a linear framework. In the closed-shell singlet manifold, although the HCCP parent molecule also converges to a linear arrangement, the halogenated derivatives present a bent nuclear configuration and correspond to halocarbenes substituted in addition by a CP group, $\text{X—C—C}\equiv\text{P}$. From these results, a few observations could be made:

- (i) When located next to a divalent and high-spin electron-deficient carbon center, electrons of the carbon–phosphorus triple bond are abundantly transferred to form a carbon–carbon bond:



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- (ii) In contrast to the situation of nitrogen counterparts XCCN, the presence of the terminal phosphorus atom allows thus a remarkable electron delocalization from which the open-shell center is actually displaced from carbon to phosphorus. The overall effect is stabilizing the triplet state, and transforming the nature of the system from a carbene to a phosphinidene.
- (iii) Stabilization of singlet carbene by a halogen atom is, as usual, large, but not large enough in this case to compete and to tip the balance in favor of the carbene character.
- (iv) The most chemically interesting implication here is that if generated in appropriate reaction conditions (without intersystem crossing), each of the high-spin and low-spin transient intermediates could exist and undergo typical and different reactions to a variety of substrates.

In an attempt to further probe the inherent duality of the CP group, namely a $C\equiv P$ substituent or a phosphorus center, we have examined and reported here a survey of the molecular and electronic structures of a selection of relevant species, in which the CP is connected to a valence-poor or electron-deficient center, including the following: NCP, PCP, NCCCP, CNCCP, PCCCP and RCCP with other types of substituents R, as well as the XCCP radicals.

COMPUTATIONAL DETAILS

All *ab initio* quantum chemical calculations were carried out using the Gaussian 98⁵ and Molcas 6⁶ suites of programs. Geometries were optimized making use of the Hartree–Fock (HF), second-order perturbation theory (MP2), coupled-cluster theory, including all singles and doubles plus perturbative corrections for the triples (CCSD(T)),⁷ as well as the popular B3LYP method⁸ of density functional theory, in conjunction with the split-valence type 6-311++G(d,p) and 6-311++G(3df,2p) basis sets, and in some cases with the correlation-consistent aug-cc-pVTZ atomic set. To construct multi-configurational wavefunctions, the complete active space CASSCF method has been used, using a natural orbital ANO-S basis set. The active spaces actually selected for variable occupancy are dependent on each system and will be mentioned separately. The stationary points were characterized by harmonic vibrational frequencies. The coupled-cluster theory CCSD(T) has been further computed with the larger 6-311++G(3df,2p) set for a few simple systems. For open-shell systems, the unrestricted formalism (UHF, UCCSD and UB3LYP) was employed. In all post-HF calculations, the core orbitals were kept frozen. Unless otherwise noted, throughout this paper, the bond distances are given in angstroms,

bond angles in degrees, relative energies and proton affinities in kcal mol^{-1} and ionization energies and electron affinities in electron-volts.

RESULTS AND DISCUSSION

NCP: Nitrene vs. Phosphinidene

The CNP system has three isomers, namely the linear NCP and CNP forms and the three-membered ring. Each isomer could exist in either a triplet or a singlet state. Our calculations confirm that the triplet linear NCP form is the most stable one. The cyclic form, either in the triplet ($^3A''$) or singlet ($^1A'$) state, can best be regarded as a cyclic carbene. In addition, they are 36 and 38 kcal mol^{-1} higher in energy than the linear triplet NCP form.^{8,9} The linear PNC isomer is also less stable, with the triplet $^3\Sigma^-$ and singlet $^1\Delta$ states lying about 14 and 25 kcal mol^{-1} higher in energy than triplet NCP, respectively. The latter isomers will not be considered further in the following section.

The linear triatomic NCP species exhibits a π^2 electron configuration: $(8\sigma)^2 (2\pi)^4 (9\sigma)^2 (3\pi)^2$, from which the triplet $^3\Sigma^-$, singlet $^1\Delta$ and $^1\Sigma^+$ states could be generated. Within a linear framework, both singlet states have the same energies. At all levels of theory considered, using either single-reference or multiconfigurational methods, the triplet $^3\Sigma^-$ state constitutes the lowest-lying form. It contains a short CN distance and a long CP distance. The distances, using different basis sets, are calculated as follows (values in Å): $r(\text{CN})/r(\text{CP})$: 1.134/1.802 at UMP2, 1.170/1.716 at UB3LYP, 1.174/1.730 at CASSCF (14,8) and 1.175/1.749 at CCSD(T). Compared with typical lengths of the $C\equiv P$ (1.54 Å) and $C=P$ (1.67 Å) bonds, these values clearly indicate that in triplet NCP the CN bond has a triplet character, whereas the CP connection is a single bond. In other words, the triplet state corresponds to a cyano-phosphinidene, $N\equiv C-P$. A similar geometry is also seen in the singlet state of NCP, in which the CN distance varies from 1.175 to 1.188 Å, whereas the CP distance ranges from 1.695 to 1.725 Å, dependent on the method employed.

The SOMOs are displayed in Fig. 1. They are classical π -orbitals. The spin density map in Fig. 1 points out that in triplet NCP, the two unpaired electrons are in fact located on the P atom, which is consistent with a phosphinidene structure.

A nitrene $N-C\equiv P$ form could not be located as a local minimum, irrespective of the method employed. All geometry optimizations starting from such structure invariably led to the phosphinidene form. The predominance of the latter can be understood by a clear-cut preference for a $C\equiv N$ bond, which is much stronger than the $C=P$ bond, as indicated by the bond energy of 212 kcal mol^{-1} for the former against that of 123 kcal mol^{-1} for the latter.¹⁰

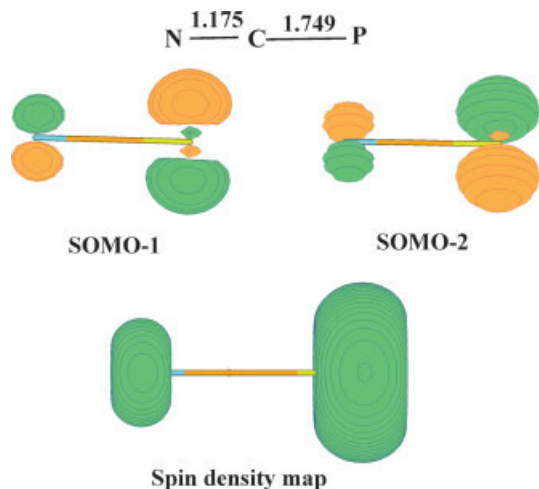


Figure 1. Shape of the SOMOs and map of spin density of the triplet $\text{NCP } ^3\Sigma^-$ (UB3LYP/6-311++G(3df,2p)). The lobes on both orbitals are in reality orthogonal, but for the sake of visibility the lobes of SOMO-2 have been significantly rotated

Regarding the singlet-triplet energy gap of cyanophosphinidene, which is the relative energy between triplet and singlet NCP, although the CCSD(T) method provides a value of 24 kcal mol^{-1} , our present CASPT2/ANO-S calculations based on CASSCF(14,8) wavefunctions suggest a value of 25 kcal mol^{-1} , which is consistent with each other.

Removal and addition of electrons are found to occur at the phosphinidene P-center of NCP. The resulting radical cation $\text{NCP}^+ (^2\Pi)$ and radical anion $\text{NCP}^- (^2\Pi)$ also have a short CN ($1.17\text{--}1.18 \text{ \AA}$) and a long CP ($1.69\text{--}1.73 \text{ \AA}$) distance. The relevant adiabatic ionization energy (IE) and electron affinity (EA) of NCP are evaluated to be: $IE_a(\text{NCP}) = 10.40 \text{ eV}$ and $EA(\text{NCP}) = 2.15 \text{ eV}$, from UB3LYP/aug-cc-pvTZ + ZPE calculations. For the IE , a similar value was given in Ref. 10 derived from CCSD(T) computations.

PCP: Cumulene vs. Phosphinidene

Geometry optimizations for the PCP molecule result in a $D_{\infty h}$ structure having two equal CP distances.¹¹ Using the UB3LYP method, the bond length of $1.625\text{--}1.628 \text{ \AA}$ is obtained in the triplet $^3\Sigma_g^-$ state, and $1.625\text{--}1.627 \text{ \AA}$ in the singlet $^1\Delta$ state. Both correspond to that of a double $\text{C}=\text{P}$ bond. The orbital configuration of the linear triplet is depicted as follows:

$$^3P=C=P^+ \quad ^3\Sigma_g^- : \dots (6\sigma_g)^2 (5\sigma_u)^2 (2\pi_u)^4 (2\pi_g)^2$$

For its part, the cyclic form is again a carbene, with a preference for the singlet 1A_1 state, which is 8 kcal mol^{-1} below the triplet state (3B_2). The singlet cycle is found at about 25 kcal mol^{-1} above the linear $^3\Sigma_g^-$ form.

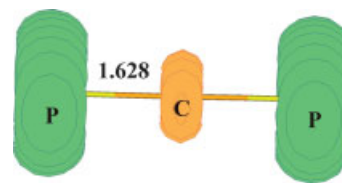


Figure 2. Map of spin density of PCP in triplet neutral $^3\Sigma_g^-$ (UB3LYP/6-311++G(3df,2p))

Calculated population analysis indicates that there is a small net charge transfer from P to C and the C atom is only slightly negatively charged (-0.13 e). On the contrary, there is a significant reorganization of the spin, which tends to enlarge the excess α -spin electron on phosphorus (1.6 e on each P-atom). The central carbon bears an excess of 1.2 e of β -spin electrons (Fig. 2).

The cumulene form persists in the radical cation and radical anion. The $\text{C}=\text{P}$ distance is compressed to 1.616 \AA upon ionization (in PCP^+) and stretched to 1.648 \AA following electron attachment (in PCP^-). In both ions, the unpaired electron is equally distributed at the two phosphorus ends. Each P atom bears an excess of 0.58α -electron, and the central carbon has an excess of 0.16β -electron.

The singlet-triplet separation, adiabatic ionization energy and electron affinity of PCP are calculated as follows: $\Delta E_{\text{ST}}(\text{PCP}) = 20 \text{ kcal mol}^{-1}$, $IE_a(\text{PCP}) = 8.78 \text{ eV}$ and $EA(\text{PCP}) = 1.86 \text{ eV}$, using the same level of theory. For IE , a similar value was reported in Ref. 11. Compared with the NCP discussed above, although the gap is slightly reduced it becomes easier to remove electrons but more difficult to generate a stable anion.

In summary, due to the molecular symmetry in PCP, a cumulenic biradical $\text{P}=\text{C}=\text{P}$ form is consistently preferred over a $\text{P}\equiv\text{C}-\text{P}$ phosphinidene (which does not exist), irrespective of the electronic state.

RCCP: Carbene vs. Phosphinidene

As stated in the introduction, the structures of the parent HCCP species and its halogenated derivatives have been investigated in much detail in earlier studies.^{1-4,12} In these four-atom compounds, the linear shape with a high spin state corresponding to an ethynyl phosphinidene is consistently the most stable arrangement. Let us examine the cases of some different R groups.

$\text{R}=\text{CH}_3$ and CF_3

In both methyl and trifluoromethyl derivatives, a similar picture emerges pointing toward a linear triplet phosphinidene ground state. The unpaired electrons are centered on the P atom (Fig. 3). The bond distances are only marginally modified upon fluoro substitution. In spite of extensive attempts making use of various methods, a bent singlet carbene structure could not be located as a local minimum. Due to the fact that the singlet counterpart of

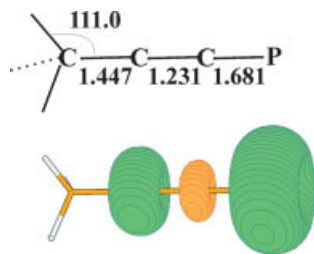


Figure 3. Geometrical parameters and maps of spin density of the triplet CH_3CCP (3A_1) using UB3LYP/6-311++G(3df,2p) calculations

linear phosphinidene, the cation and the anion are subject to a complex Jahn–Teller distortion, they are not considered in detail here.

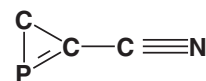
$\text{R}=\text{C}_6\text{H}_5$

Similar to the methyl case, the phenyl group leads to a triplet phosphinidene with a C_{2v} symmetry. Apart from the ring, its geometrical parameters differ from those methyl counterparts, namely with the values of 1.407, 1.240 and 1.669 Å for the C—C, C≡C and C—P distances, respectively. Again, no bent singlet carbene structure could be optimized. Upon ionization and electron attachment, the C_{2v} and linear CCP framework remains unchanged. The singlet–triplet gap, adiabatic ionization energy and electron affinity of PhCCP are calculated as follows: ΔE_{ST} (PhCCP) = 22 kcal mol $^{-1}$ using CCSD(T)/6-311 + G(d,p) and IE_{a} (PhCCP) = 7.9 eV and EA (PhCCP) = 1.8 eV using the UB3LYP/6-311++G(3df,2p) + ZPE calculations.

$\text{R}=\text{CN}$

The potential energy surface (PES) of the C_3NP molecular system contains no less than 30 local minima, excluding possible fragments. A separate rapid mapping of the PES at the UB3LYP/6-311 + G(d,p) + ZPE level indicates that the equilibrium structures include four linear forms, seven bent open-chain structures and several three-membered rings, bicycles and cages. It is not our intention to explore this PES in detail. We only note that in the triplet manifold the linear triplet NCCCP form turns out to be the most stable form, the energy of the latter being 25, 50 and 65 kcal mol $^{-1}$ below those of the linear isomers CNCCP, CCCNP and CCNCP, respectively.

On the singlet PES, a three-membered ring actually corresponding to a cyano-substituted cyclic carbene, as displayed in Scheme 1, is found to be the energetically lowest-lying singlet isomer. It is about 4 kcal mol $^{-1}$ below the linear NCCCP but 17 kcal mol $^{-1}$ above the linear triplet NCCCP. In other words, the linear triplet NCCCP species is the global minimum of the C_3NP super system.



Scheme 1

The NCCCP species formally contains two CN and CP groups, both connected to a central carbon atom. Such a divalent carbon suggests a bent carbene structure. Nevertheless, geometry optimizations consistently end up in a linear skeleton, irrespective of the electronic state. No bent carbene could be identified as the equilibrium structure. In its $^3\Sigma^-$ state, the four distances of NCCCP are calculated as follows: NC, 1.165 Å; CC, 1.246 Å; CC, 1.343 Å; CP, 1.654 Å (values obtained from UB3LYP/6-311 + G(3df,2p)).

The atomic spin densities are calculated to be 0.39 (N), −0.22 (C), 0.82 (C), −0.42 (C) and 1.42 (P); a negative value stands for an excess of β -spin electrons. The unpaired electrons are mostly centered at the terminal P-atom and, to a lesser extent, the central carbon. This electron distribution suggests the importance of the following resonance structures: (i) phosphinidene $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{P}^\bullet$; (ii) cumulene biradical $\text{N}\equiv\text{C}-\text{C}^\bullet=\text{C}=\text{P}^\bullet$; (iii) biradical $\text{N}=\text{C}=\text{C}^\bullet=\text{C}=\text{P}^\bullet$. Analysis of the corresponding CASSCF wavefunction points out that form (i) is predominant.

The isocyano isomer CNCCP also exhibits a linear geometry and a $^3\Sigma^-$ ground state. In many aspects, the electron distribution of the latter is close to that of NCCCP, showing thus a phosphinidene form $\text{C}\equiv\text{N}-\text{C}\equiv\text{C}-\text{P}^\bullet$. As mentioned above, the relative energy between both cyano and isocyano forms amounts to 25 kcal mol $^{-1}$ in favour of the former.

Both the corresponding cation NCCCP^+ ($^2\Pi$) and anion NCCCP^- ($^2\Pi$) radicals keep the linear framework. Electron removal or incorporation occurs at the P atom; as a consequence, the unpaired electron of the resulting ion is centered on P, and the vertical ion is not far from the adiabatic one. The energy gain following geometry relaxation in both ions is not large, being at most 0.02 eV.

The singlet–triplet gap, adiabatic ionization energy and electron affinity are evaluated as follows: ΔE_{ST} (NCCCP) = 9 kcal mol $^{-1}$ using CASPT2/ANO-S and IE_{a} (NCCCP) = 9.4 eV and EA (NCCCP) = 2.5 eV using the UB3LYP/6-311++G(3df,2p) + ZPE calculations. The lowest-lying quintet state of this isomer is bent ($^5A'$) and located at about 4.1 eV above the ground triplet state. This phosphinidene possesses thus a significantly higher IE but also a substantial EA .

$\text{R}=\text{CP}$

As in the cases of PCP and NCCCN^{13,14} the presence of two CP groups gives rise to a centro-symmetric linear geometry. In the triplet ground state $^3\Sigma_g^-$, the CP distance is markedly compressed, namely being 1.609 Å

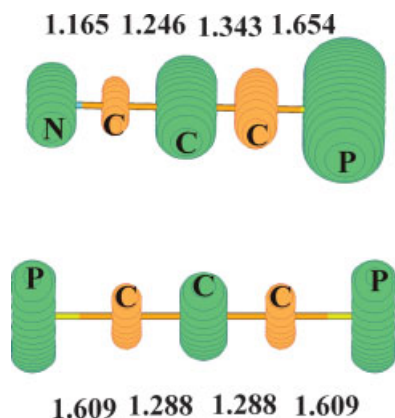


Figure 4. Maps of spin densities of the triplet NCCCP ($^3\Sigma^-$) and PCCCP ($^3\Sigma_g^-$) from UB3LYP/6-311++G(3df,2p) calculations

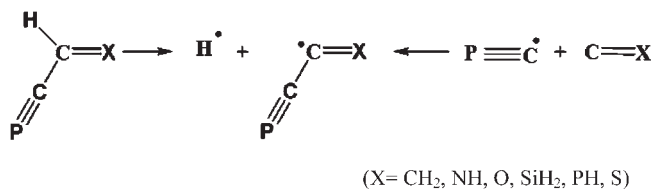
compared with 1.654 Å in NCCCP. On the other hand, the CC distance of 1.228 Å lies in-between the values of 1.246 and 1.343 Å given above for the cyano derivative. The calculated spin densities amount to 1.0 (P), -0.35 (C) and 0.70 (central C). This corresponds well to a cumulenetic biradical $\text{P}=\text{C}=\text{C}=\text{C}=\text{P}$, even though the central carbon bears a substantial concentration of α -spin excess. A similar result has been obtained for $\text{C}(\text{CN})_2$ (Ref. 13). The difference between NCCCP and PCCCP can be illustrated vividly in the maps of spin densities (Fig. 4).

The singlet–triplet gap, adiabatic ionization energy and electron affinity are evaluated as follows: ΔE_{ST} (PCCCP) = 2 kcal mol $^{-1}$ from CASPT2/ANO-S and IE_{a} (PCCCP) = 8.3 eV and EA (PCCCP) = 2.3 eV using the UB3LYP/6-311++G(3df,2p). All values were corrected for ZPEs. Accordingly, this cumulenetic biradical has a small singlet–triplet energy gap. Within the accuracy of the methods employed, both singlet and triplet states could be considered as nearly degenerate.

In summary, in spite of the fact that the RCCP molecule bears a central divalent carbon atom connected to two R and CP groups, none of the derivatives examined here actually behave as a carbene. In most cases, the ground electronic structure corresponds to the triplet state of an ethynyl-phosphinidene. In $\text{C}(\text{CP})_2$, the molecular symmetry tends to impose a cumulenetic biradical structure. Again, this emphasizes the high mobility of π -CP electrons that readily delocalize into adjacent electron-deficient centres.

XCCP with X = CH $_2$, NH, O, SiH $_2$, PH and S: C vs. P radical

In this last section, we turn our attention to a different case involving a doublet ground state. Let us consider the process depicted in Scheme 2. On the one hand, abstraction of the hydrogen atom or a C–H bond cleavage of a



Scheme 2

ketone (X=O) molecule leads to an initial carbon-centered radical. This radical can also be formed by addition of the CP radical into a CX substrate, including the stable HNC, CO and CS molecules. In view of the fact that several C_nP , C_nS and C_nN species have been detected in interstellar space,^{15,16} they could encounter each other or react with oxygen atoms to generate these radicals. In other words, these radicals are of interest in the interstellar and atmospheric chemistry.

It is not our intention to explore the PESs of these species. Each of them contains several possible isomers and interconnection pathways. For example, in the simplest species SCCP, one can count at least seven possible isomers and a large number of possible fragments. A rapid mapping of this PES points out that the SCCP arrangement is by far the most favoured one, the other isomers (CCPS, CSCP, CCSP...) being at least 50 kcal mol $^{-1}$ higher in energy.

Geometry optimizations using different levels of theory, including UHF, UMP2, UCCSD(T), CASSCF and UB3LYP with various basis sets, invariably end up in a linear SCCP structure. The lowest bending mode is characterized by a small but positive vibrational frequency of around 150 cm $^{-1}$. The same trend is found for other XCCP radicals whose optimized geometrical parameters are displayed in Fig. 5. The

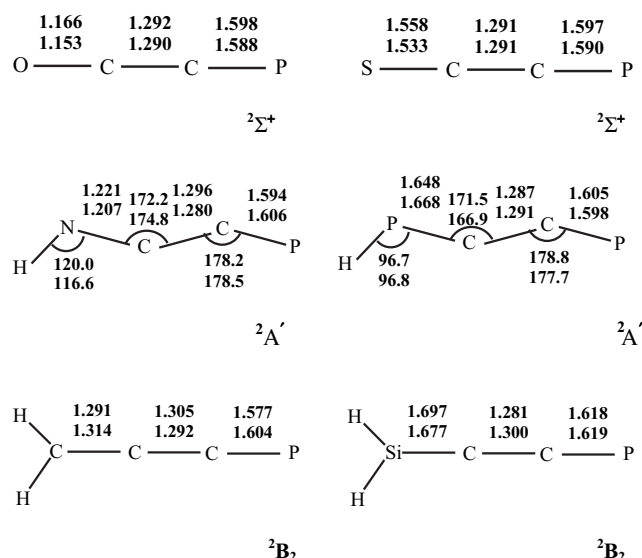


Figure 5. Optimized geometrical parameters of the XCCP radicals: upper values, B3LYP/6-311++G(3df,2p); lower values, CASSCF(14,8)/ANO-S

Table 1. Ionization energies and electron affinities for structures with a doublet ground state

Structures	IE_a (eV)	EA_a (eV)
OCCP	7.9	1.2
SCCP	7.7	1.6
H ₂ CCCP	8.2	1.5
H ₂ SiCCP	8.1	1.9
HNCCP	7.4	1.3
HPCCP	8.3	2.0

asymmetrical HNCCP and HPCCP species exhibit open-chain skeletons.

The CP bond length amounts to 1.60–1.62 Å in all cases considered, whereas the central CC distance is in the range of 1.27–1.30 Å and is dependent on the methods employed. The CP distance is thus between that of a triple (1.53 Å) and a double (1.65 Å) carbon–phosphorus bond.

In the linear SCCP species, the unpaired electron is found to mainly be located at the P atom (0.66 e). However, the other atoms also have a significant excess α -spin electron, namely S (0.39 e), (S) C (0.36 e), thanks to a large transfer from the (P) C atom (−0.42 e). The excess α -spin electron at P is reinforced in other XCCP radicals, amounting up to 0.9 e. In this context, it is reasonable to consider these as P-radicals, $X=C=C=P$, rather than C-radicals, $X=C^{\cdot}-C\equiv P$. This is in clear contrast with the isovalent CN group, which invariably remains as a cyano $C\equiv N$ substituent.

The adiabatic ionization energies and electron affinities are evaluated using the UB3LYP/6-311++G(3df,2p)+ZPE calculations. It appears that a XCCP species bearing a second-row X atom is characterized by a larger electron affinity than its first-row counterpart. The results are shown in Table 1.

In conclusion, the structures studied in this work demonstrate that when connected to a valence-deficient center (triplet or radical), π -electrons of the terminal CP group tend to move into other parts of the system, thus transforming it into a P-triplet or P-radical. It is known that there is only a marginal difference in the electronegativity of C and P atoms in favor of C. Apparently, the electrons tend to be attracted from P through C in such a way that a CP group does not behave as a phosphaehtynyl substituent, but rather as a P-centered phosphinidene or radical due to a vigorous electron delocalization. The C

atoms behave as a point of passage for a through-bond electron transfer between P and other molecular parts.

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