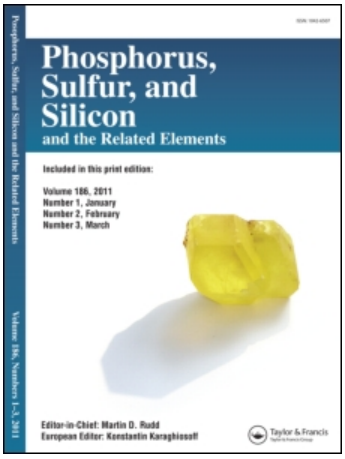

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The Electronic Nature of the P=C Bond

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THE ELECTRONIC NATURE OF THE P=C BOND

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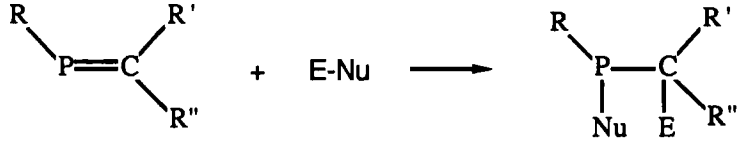
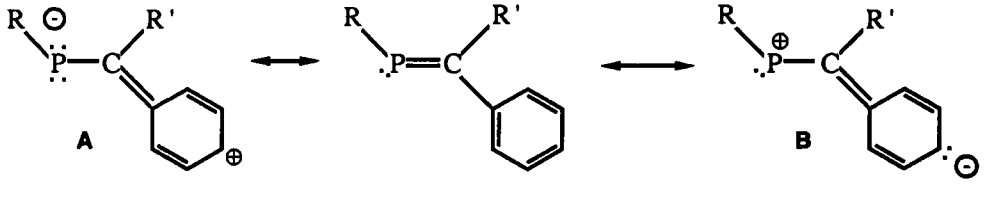
Abstract The influence of substituents at the carbon of the P=C bond of about 60 phosphaalkenes was investigated by ^{31}P NMR spectroscopy. The P=C system is characterized as electronwithdrawing. All compounds were found to be configurationally stable.

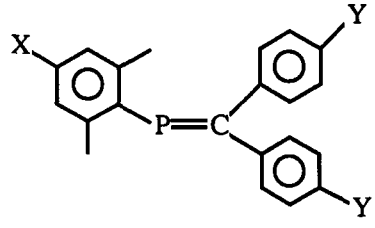
The phosphorus carbon double bond (P=C) of phosphaalkenes is of considerable interest. In comparison to the analogous imino (N=C) and carbonyl group (O=C), one would expect that its polarization should be reversed, as nitrogen and oxygen are more electronegative than carbon, whereas phosphorus is less electronegative. Indeed, in agreement with this qualitative reasoning and with theoretical calculations, experiment shows the expected polarity: in general, electrophiles (E) were found to add to carbon and nucleophiles (Nu) to phosphorus.



In contrast with this observation, it is known that heteroatoms at carbon stabilize the phosphaalkene by conjugation. The phenyl group is an even more informative indicator as, in principle, it can donate or accept electrons in response to a substituent, as illustrated for the P=C group.

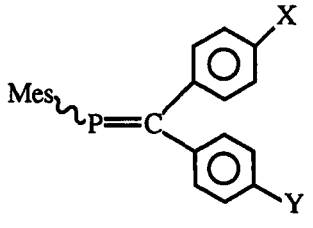


We have shown in a preliminary paper[1] that contrary to its "natural" polarization, the P=C groups does indeed act as an electronwithdrawing substituent towards the phenyl group, in other words, resonance structure **A** is important, while structure **B** is not. We have now extended our previous investigation to a total number of 50 substituted triarylphosphaethenes **1-4** and to several phosphaalkenes which have aliphatic substituents at carbon (*vide infra*).



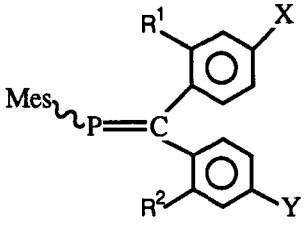
1

X = Me; Y = H, CN, CF_3, Br, Me, OMe, NMe_2
X = MeO; Y = H, Br, NMe_2



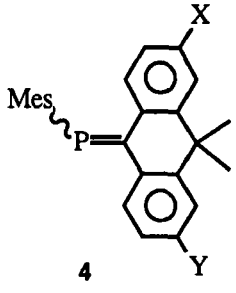
2

X, Y = H, CN, Br, F, Me, OMe, NMe_2, CN, Br



3

R^1, R^2 = H, Me, Et, *i*-Pr
X, Y = H (Br, OMe)



4

X = H,
Y = H, Br, OMe

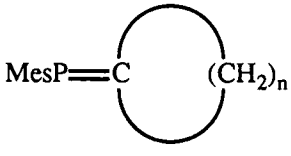
The synthesis of **1-4** was achieved by coupling the lithium phosphides ArPHLi with the appropriate ketones[1] according to the method of Becker[2]. In the case of unsymmetrical ketones, the expected *E/Z*-isomers of the phosphaalkene were obtained. They have different phosphorus chemical shifts; their ratio is 1:1 for **2** and depends on R^1 and R^2 for **3**.

The substituent effects on $\delta(^{31}P)$ were found to be additive. They obey a Hammett-type relation: when one relates $\Delta\delta$ to the shift of the parent compound (**1**, X = Y = H: $\delta(^{31}P)$ = 234.5 ppm), one finds that $\Delta\delta = C\cdot\sigma$. Similar relationships have been reported for other C=X combinations with X = ^{13}C, ^{17}O or ^{15}N. However, the constant C is not equal for the *E*- and the *Z*-substituent : it is larger for *E* and smaller for *Z*. We were able to obtain from the mixture of stereoisomers of **2** (X = Br, Y = OMe) crystals

of the Z-isomer; an X-ray crystal structure allowed the stereochemical assignment to the two series. It turned out that in general, the conjugative effect of the *trans*-substituent is larger, which can be explained by the better coplanarity of its benzene ring with the P=C system. In line with this reasoning, *ortho*-substituted derivatives **3** show deshielded $\delta(^{31}P)$, especially when the *ortho*-substituent is in the *Z*-position, because in this case, steric crowding prevents the phenyl groups from attaining coplanarity. This also tells us that the phenyl group, if allowed to be coplanar with the P=C system, donates electron density to the latter (cf. structure **A**). An X-ray crystal structure of *E*-**3** (R^1 = X = Y = H, R^2 = *i*-Pr) supports the stereochemical assignments[3]. Correspondingly, compounds **4** have a more shielded ^{31}P, because the benzene rings are forced more or less into a coplanar arrangement.

The linearity of the Hammett plot implies that the conformations of all phosphaalkenes **1** and **2** in solution are approximately equal; apparently, they are governed largely by steric factors and hardly by electronic effects. On the basis of a Swain-Lupton analysis ($\Delta\delta = f \cdot F + r \cdot R$), it was tentatively shown that the conformational angles in solution are smaller than those observed in the crystal. The crystal structures reveal a a considerable variation in torsional angles of the C-aryl groups; this confirms that torsional angles - though relevant for mesomeric interactions with the P=C bond - are of minor energetic importance. An analysis of *meta*-^1H and *para*-^{13}C chemical shifts of several **1** and **2** permitted the determination of the Hammett σ (*E*-MesP=C-) to be about 0.25, characterizing this functional group as weakly electronwithdrawing (like Cl or Br). However, other factors are probably also contributing to δ, such as anisotropy, the *E/Z*-configuration of the substituent-bearing phenyl ring, and the bond angles at the P=C bond.

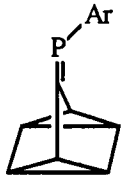
Besides a number of phosphaalkenes substituted at carbon by both an aryl and alkyl group, also the dialkyl substituted derivatives **5-13** ($\delta(^{31}P)$ in ppm between brackets) were prepared.



5 : n = 3 (δ = 199.7)
6 : n = 4 (δ = 197.9)
7 : n = 6 (δ = 196.8)

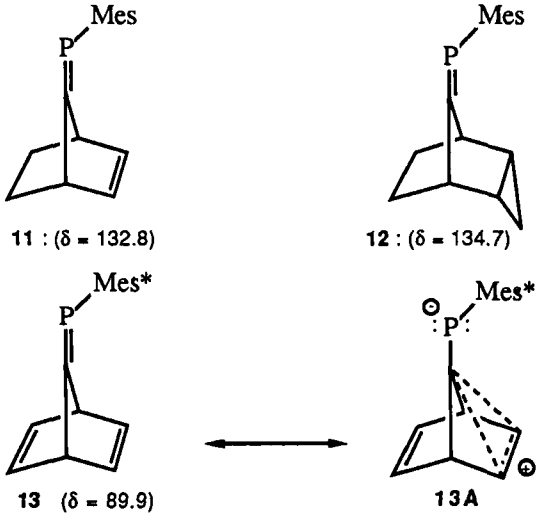
MesP = (2-Ad)

8 : (δ = 179.1)



9 : Ar = Mes (δ = 175.1)
10 : Ar = Mes * (δ = 189.9)

The simple cycloalkylidene derivatives **5-7** show only a small dependence of $\delta(^{31}P)$ on ring size, as do analogous cycloalkanones and methylenecycloalkanes. Of special interest are the polycyclic phosphaalkenes, in particular the couple **10** and **13**. The strong shielding of $\Delta\delta$ = 100 ppm is taken as evidence for a contribution of resonance structure **13A**; it again confirms the electronwithdrawing nature of the P=C system.



11 : (δ = 132.8) **12** : (δ = 134.7)

13 (δ = 89.9) **13A**

Interestingly, none of the phosphaalkenes showed purely thermal *cis/trans*-isomerization. In **2**, a catalyzed *cis/trans*-isomerization was sometimes observed. It was probably caused by minute amounts of an as yet unidentified catalyst which is consumed after some time; afterwards, the isomerization stops, from which one can derive that the isomerization barrier is greater than 30 kcal·mol^{-1}. Even **13**, with its strongly weakened double bond, did not isomerize; ^{1}H-NMR magnetization transfer experiments allow the estimate of $\Delta G^{\neq}_{378} > 23$ kcal·mol^{-1} for this process, indicating that the π-component of this P=C bond is stronger than at least 23 kcal·mol^{-1}.

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