The Substituent Effect of the Phosphaalkenyl Group

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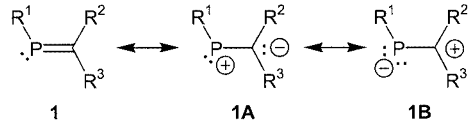
Several novel phosphaalkenes (*E*)-Mes*P=CHC$_6$H$_4$X (**6**; X = Me$_3$Si, Me$_3$Sn, CHO, COOH, CN) were prepared and, together with other known members of this series, subjected to an analysis of linear free-energy relationships based on the values of pK_a and values of δ(^{13}C$_{para}$) of substituted benzoic acids and on the values of δ(^{13}C$_{para}$) of substituted bromobenzenes. These analyses indicate that the (*E*)-Mes*P=CH group is a weak electron donor with a predominantly inductive effect (σ_p = –0.1) on a neighboring benzene ring; resonance interactions are of minor importance. This result shows that the P=C bond is surprisingly analogous to the C=C bond, and thus confirms the well-known diagonal relationship in the Periodic System between carbon and phosphorus atoms. The relationship between X and the values of δ(^{31}P) of **6** is quite pronounced. It confirms the dominance of inductive interactions on the value of δ(^{31}P); only with strongly electron-donating substituents may a certain degree of resonance interaction be involved.

Introduction

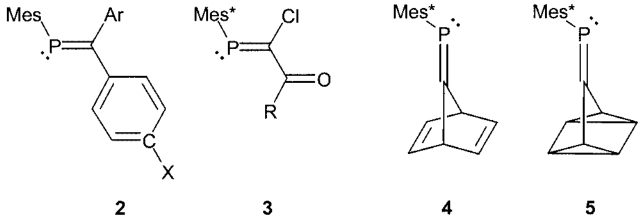
The classical double bond rule states that elements of the third and higher periods lack the ability to form stable compounds involving pπ–pπ bonds analogous to the C=C double bond of alkenes.[1,2] According to this rule, phosphaalkenes R^{1}P=CR^{2}R^3 (**1**) are expected to be chemically quite different from alkenes, and indeed they are, for example, as far as ease of preparation or thermal stability are concerned; special precautions such as steric protection or resonance stabilization of the P=C bond are required to ensure their viability under ordinary conditions.[3–5]

Another potential difference between the two types of double bonds is their electronic structure, in particular the polarization. Apart from substituent effects, the C=C bond is inherently nonpolar. For phosphaalkenes, the situation may be different because the two elements differ in electronegativity χ,[6–9] with phosphorus being more electropositive than carbon [on the Pauling scale:[6] χ(P) = 2.1, χ(C) = 2.5]. Consequently, one would predict **1** to be polarized as indicated by the resonance structure **1A** and not according to **1B** (Scheme 1). In line with this assumption, phosphaalkenes react with polar reagents by attack of a nucleophile at the phosphorus atom or of an electrophile at the carbon atom;[3–5] this regiochemistry is opposite to that of C=O and C=N bonds as oxygen and nitrogen atoms are more electronegative than carbon atoms.



Scheme 1

To clarify the question of the polarity of the P=C bond, we had earlier investigated the ^{31}P and ^{13}C chemical shifts of several triarylphosphaalkenes[10,11] **2** as well as NMR, UV, and IR spectra and X-ray crystal structures of β-phosphaenones[12] **3** (Scheme 2). For **2** (Mes = 2,4,6-trimethylphenyl), the values of δ(^{13}C$_{para}$) of the aryl carbon atoms *para* to the MesP=C group (shown in Scheme 2) suggest that this group has a Hammett σ value of ca. 0.2. This result was unexpected as it would mean that contrary to the "natural" polarization as indicated by resonance structure **1A**, the group is slightly electron-withdrawing; this phenomenon would be more in line with **1B**. A calculational analysis[12] of the results obtained for **3** (Mes* =



Scheme 2

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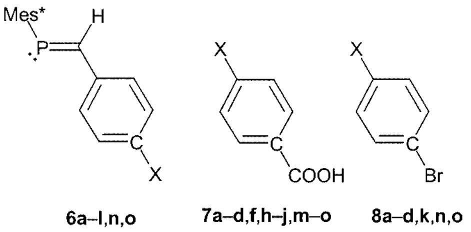
2,4,6-tri-*tert*-butylphenyl = supermesityl), and of the spectacular shielding[11] of the phosphorus atom in **4** [$\delta(^{31}P) = 89.9$] as compared to **5** [$\delta(^{31}P) = 189.9$], revealed that several factors play a role and that the situation is far from clear-cut.

For this reason, we decided to extend the range of phosphaalkenes to investigate additional Hammett-type linear free-energy relations.[13–16]

Results and Discussion

We concentrated our investigations on the phosphaalkenes **6** that are rather stable because they are protected by the bulky supermesityl group Mes* at the phosphorus atom (Scheme 3; they are arranged in the order of increasing σ_p of the *para* substituent X). Correlations were derived with Hammett σ_p or σ_p^+ values[15,16] and with σ_p^n values[16–19] for values of pK_a of benzoic acids, for the values of $\delta(^{13}C_{para})$ of the *para*-carbon atoms of substituted benzoic acids (**6l** and **7**) and of bromobenzenes (**6j** and **8**), and for the values of $\delta(^{31}P)$ of the P=C bond of **6**.

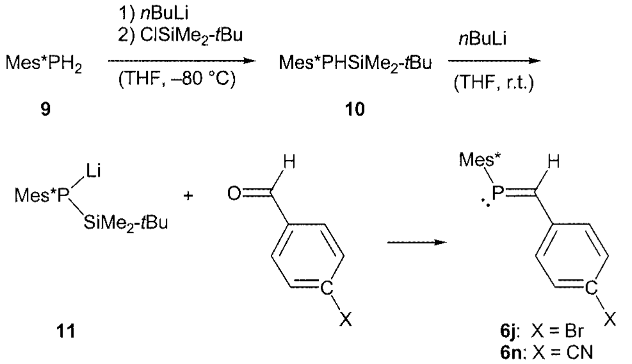


a: X = NMe_2
b: X = OH
c: X = OMe
d: X = Me
e: X = $SiMe_3$
f: X = H
g: X = $SnMe_3$
h: X = F
i: X = Cl
j: X = Br
k: X = CHO
l: X = COOH
m: X = CF_3
n: X = CN
o: X = NO_2

Scheme 3

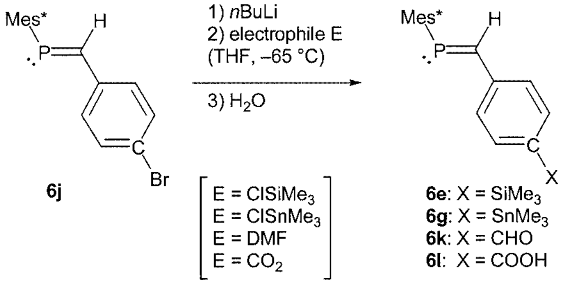
Synthesis of (*E*)-Mes*P=CHAr (6)

Several of the phosphaalkenes **6** have already been prepared by a number of different approaches.[3–5] This observation holds for the unsubstituted parent compound **6f**[20–23] and for **6a**,[21–23] **6b**,[22] **6c**,[21,22,24] **6d**,[23] **6g**,[23] **6h**,[22] **6i**,[22,24] **6j**,[22] and **6o**.[24] Using the method of Yoshifuji et al.,[20] we obtained **6j** and **6n** in a one-pot procedure by conversion of Mes*PH_2 (**9**) via the silyl derivative **10** into its lithio derivative **11**, which was treated with *p*-bromo- or *p*-cyanobenzaldehyde to furnish **6j** or **6n**, respectively, in yields of 90–95% (Scheme 4). This reaction was stereospecific in providing the (*E*) isomer exclusively.



Scheme 4

Compound **6j** served as starting material for the synthesis of **6e**,**g**,**k**,**l** as shown in Scheme 5. In THF at −65 °C, **6j** was treated with *n*-butyllithium, and the resulting aryllithium intermediate was quenched with electrophilic reagents E (E = $ClSiMe_3$, $ClSnMe_3$, dimethyl formamide, or CO_2, respectively). Again, the yields were high (about 95%).



Scheme 5

Linear Free-Energy Relationships

The original Hammett Equation (1)[13] defines the influence of substituents on the acidity of benzoic acids where K is the dissociation constant of the acid, σ_X is a measure of the electron-donating or -withdrawing effect of the substituent X, and ρ is the reaction constant; by definition, $\rho = 1$ in aqueous solution. In general, ρ is a measure of the sensitivity of the property under investigation towards substituent effects.

$$\sigma_X \cdot \rho = \log K_X - \log K_H \qquad (1)$$

For this reason, we first determined the acidity of substituted benzoic acids **7**. As most of these acids were insufficiently soluble in water, the value of pK_a was determined in 85.6% ethanol/water by titration with NaOH (Table 1). It should be noted that the value of pK_a is strongly dependent on the solvent;[15] in more polar solvents, the dissociation constant is increased, as is illustrated by the values for the unsubstituted parent, benzoic acid (**7f**), which are pK_a(water[25]) = 4.19 and pK_a(85.6% ethanol/water) = 6.88. Similarly, the reaction constant for the dissociation is (by definition[13]) $\rho = 1$ in water, and $\rho = 1.57$ in ethanol.[26]

Table 1. Values of pK_a of benzoic acids **7** in 85.6% ethanol/water

Compound	X	σ_p	σ_p^+	σ^n	pK_a
7a	NMe_2	−0.83	−1.70	−0.17	7.88
7b	OH	−0.37	−0.92	−0.18	7.45
7c	OMe	−0.27	−0.78	−0.11	7.15
7d	Me	−0.17	−0.31	−0.13	7.13
7f	H	0.00	0.00	0.00	6.96
7h	F	0.06	−0.07	0.06	6.62
7i	Cl	0.23	0.11	0.24	6.44
7j	Br	0.23	0.15	0.26	6.39
7m	CF_3	0.54	0.61	0.53	6.02
7n	CN	0.66	0.66	0.67	5.69

The Hammett plot for 85.6% ethanol/water yields Equations (2), (3), and (4) for σ_p, σ_p^+, and σ_p^n, respectively, where σ_p is the "normal" substituent constant for the dissociation of benzoic acids; it is mainly dependent on inductive effects of the substituent,[15,16] whereas σ_p^+ is appropriate in the case of through-conjugation, when strong electron demand is involved.[15,16] In contrast, σ^n has been derived for systems that lack conjugative interactions and is supposed to reflect purely inductive effects.[16,19] Only the plot for σ_p is shown in Figure 1.

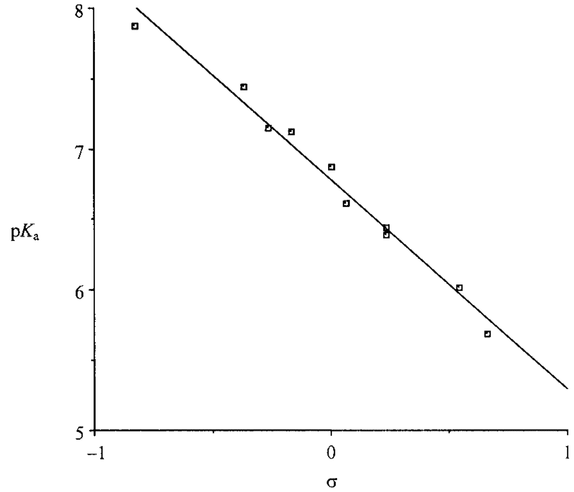


Figure 1. Hammett plot for values of pK_a of **7**

$$\mathrm{p}K_a = 6.78 - 1.49\sigma_p\ (R = 0.982) \tag{2}$$

$$\mathrm{p}K_a = 6.57 - 0.88\sigma_p^+\ (R = 0.919) \tag{3}$$

$$\mathrm{p}K_a = 7.02 - 2.11\sigma^n\ (R = 0.904) \tag{4}$$

Clearly, the fit for σ_p^+ and σ^n is less satisfactory. Furthermore, Equation (2) furnishes $\rho(\sigma_p) = 1.49$, which, in line with expectation, is close to, but slightly smaller than, the value[26] in pure ethanol (1.57); in contrast, $\rho(\sigma_p^+) = 0.88$ is *smaller* and $\rho(\sigma^n)$ very much larger than the value in water, a situation that may be considered as additional evidence against their validity in the present context. These observations confirm the conclusion that the dissociation of benzoic acids is largely determined by general inductive effects of the substituent X and that resonance effects are of minor importance.[15,16]

Insertion of pK_a(**6l**) = 6.88 into Equation (2) yields σ_p(Mes*P=CH) = −0.12. This result was surprising as it characterizes the phosphaalkenyl group as a weak electron donor, which is in line with its "reactivity pattern" and with the resonance structure **1A** mentioned in the Introduction, but it is opposite to the value of σ = 0.2 reported[11,12] for **2** and to a contribution by structure **1B**.

Another indicator that has been used frequently to determine substituent effects are NMR spectroscopic chemical shifts, in particular values of $\delta(^{13}C_{para})$ of the carbon atoms *para* to the substituent X (see Scheme 2; Table 2).[14−16,27−30] For the benzoic acids **6l** and **7**, the values were obtained in [D$_6$]DMSO because many compounds **7** are insufficiently soluble in $CDCl_3$; spectra of the bromobenzenes **6j** and **8** were measured in $CDCl_3$.

Like the values of pK_a, the correlations of the values of $\delta(^{13}C_{para})$ are sensitive to solvent polarity and solvation, factors that determine the relative contribution of inductive effects, normally correlated with σ_p values, and resonance effects, which correlate with σ_p^+. Empirically, the correlation of values of $\delta(^{13}C_{para})$ with those of σ_p^+ appears to give the best fit,[14,28−30] but there is extensive discussion in the literature concerning the reasons for this empirical observation.[16] From the data in Table 2, we, too, find the best fit for σ_p^+. Equation (5) gives the correlation of σ_p^+ for **7** (Figure 2) and Equation (6) for **8** (Figure 3). The correlations for σ_p were less satisfactory (R = 0.93 and 0.92, respectively).

$$\mathbf{7}\text{: } \delta(^{13}C_{para}) = 129.36 + 8.09\sigma_p^+\ (R = 0.977) \tag{5}$$

$$\mathbf{8}\text{: } \delta(^{13}C_{para}) = 122.10 + 9.10\sigma_p^+\ (R = 0.981) \tag{6}$$

When inserted into Equation (5), the value for **6l** [$\delta(^{13}C_{para})$ = 128.54 ppm] furnishes σ_p^+(Mes*P=CH) = −0.12, and similarly from Equation (6), **6j** [$\delta(^{13}C_{para})$ = 121.58 ppm] yields σ_p^+(Mes*P=CH) = −0.06. These values are in surprisingly good agreement with σ_p(Mes*P=CH) = −0.12 from the pK_a experiments. The values are rather small, however, and if one considers the (less reliable!) σ_p values (**6l**: 0.09; **6j**: 0.11), one comes to the conclusion that the electronic effect of the phosphalkenyl group is slightly electron-donating, but close to zero. A comparison with the vinyl group [σ_p(CH_2=CH) = −0.04; σ_p^+(CH_2=CH)[15] = −0.12] shows that the effect of the C=C bond is very similar, with both P=C and C=C having only weak interactions with a benzene ring. This feature is in line with the old empirical "diagonal relationship" between elements of the second and third periods that predicts, inter alia, similarities between carbon and phosphorus atoms;[31] applied to low-coordinate systems, such as (phospha)alkenes Y=C with Y = C or P, this similarity

Table 2. Chemical shifts $\delta(^{31}P)$ of **6** and $\delta(^{13}C_{para})$ of substituted benzenes **7** and **8**

Compound	X	σ_p	$\sigma_p{}^+$	σ^n	**6** $\delta(^{31}P)$[a]	**7** $\delta(^{13}C_{para})$[b][c]	**8** $\delta(^{13}C_{para})$[a][b]
a	NMe_2	−0.83	−1.70	−0.17	233	116.7	108.3
b	OH	−0.37	−0.92	−0.18	244	121.1	113.4
c	OMe	−0.27	−0.78	−0.11	248	122.7	112.6
d	Me	−0.17	−0.31	−0.13	254	127.8	119.1
e	$SiMe_3$	−0.07	0.02	–	262.3	–	–
f	H	0.00	0.00	0.00	259	130.6	122.6
g	$SnMe_3$	0.00	−0.12	–	260.7	–	–
h	F	0.06	−0.07	0.06	257	127.4	–
i	Cl	0.23	0.11	0.24	264	129.3	–
j	Br	0.23	0.15	0.26	264.4	129.8	–
k	CHO	0.42	0.73	–	283.1	–	129.4
l	COOH	0.45	0.42	0.41	279.4	–	–
m	CF_3	0.54	0.61	0.53	–	135.4	–
n	CN	0.66	0.66	0.67	283.9	134.6	127.8
o	NO_2	0.78	0.79	0.78	284.6[c][d]	136.0	129.7

[a] In $CDCl_3$, unless otherwise stated. [b] *para*-C relative to X; see Scheme 3. [c] In $[D_6]$DMSO. [d] From ref.[24]

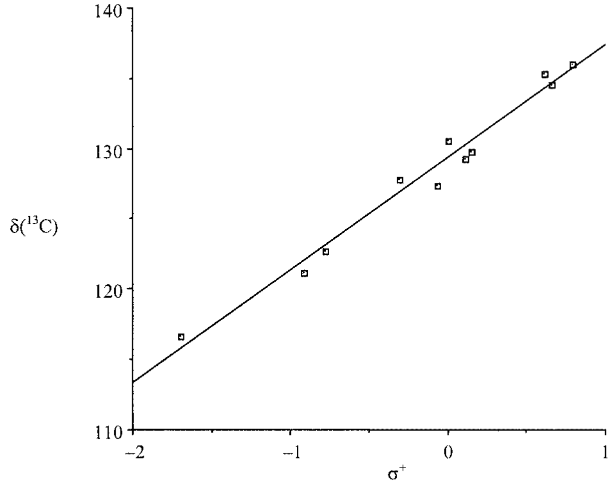


Figure 2. Hammett plot for values of $\delta(^{13}C_{para})$ of **7**

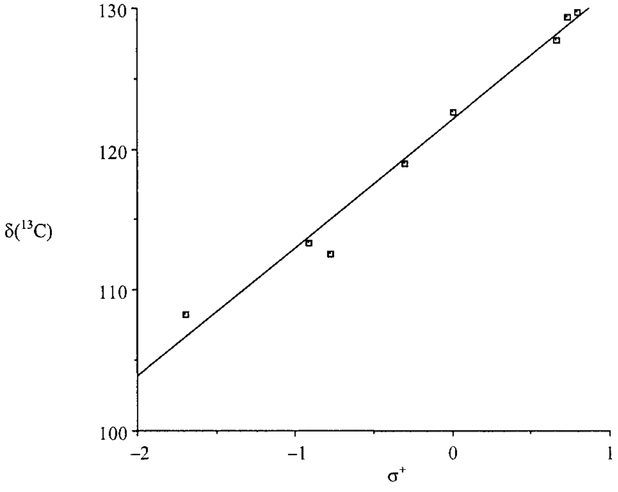


Figure 3. Hammett plot for values of $\delta(^{13}C_{para})$ of **8**

has been expressed succinctly in the title of the recent overview, "Phosphorus: The Carbon Copy".[4]

Apparently, the slight electron-donating character of the P=C group that is expected from its overall polarization, with more electron density at the carbon atom adjacent to the benzene ring, is partly counteracted by a resonance effect as expressed by **1B**. While the carbon atom in **1B** and the phosphorus atom in **1A** are both positively charged and formally both have six electrons, the *tricoordinate* carbon atom is energetically less unfavorable than the *dicoordinate* phosphorus atom. Moreover, as calculations for the β-phosphaenones[12] **3** and for their carbon analogue, acrolein,[32,33] have shown, resonance effects in the π-system of this type of double bond system tend to be (partially) compensated by opposite electron shifts in the σ-system. For the unsubstituted parent phosphaalkene $HP{=}CH_2$, ab initio SCF calculations suggest that its π bond is only slightly polarized towards the carbon atom; the main contribution to the $^{\delta+}P{-}C^{\delta-}$ polarization finds its origin in the σ bond.[34,35]

In view of this low electronic profile of the P=C group, it seems risky to speculate about the difference between our results obtained for **6** ($\sigma_p \approx -0.1$) and those reported for **2** ($\sigma_p \approx 0.2$).[11,12] Presumably, differences in the structure, such as the additional aryl group in **2** and the degree of coplanarity of the aryl groups resulting from steric crowding,[3−5,10,11,22] are sufficient to cause the observed small changes in electronic character.

Finally, having a considerable number of phosphaalkenes **6** available, we investigated also the Hammett-type influence of the substituents X on values of $\delta(^{31}P)$. Previous work on **2** has revealed[3−5,10,11] that the phosphorus chemical shift is rather sensitive to substituents at the double bond and that electron-donating substituents lead to increased shielding of the phosphorus nucleus. Although this observation seems to be in agreement with a contribution from resonance structure **1B**, it may also signal an extreme sensitivity to small changes resulting from inductive effects.

The Hammett relations according to Equations (7), (8), and (9) were derived from Table 2 and Figure 4. In this case, the correlations are poorer than in the other Hammett relations reported so far; the correlation for σ_p, however, is the best of the three. Moreover, in Equation (7), the reference value $\delta(^{31}P) = 259.8$ ppm is practically identical to that of the parent compound **6f** [$\delta(^{31}P) = 259.0$ ppm], whereas Equations (8) and (9) yield $\delta(^{31}P) = 264.3$ and 253.3 ppm, respectively. We feel, therefore, that here, as in the case of the values of pK_a of **6**, the correlation with σ_p is the more appropriate one.

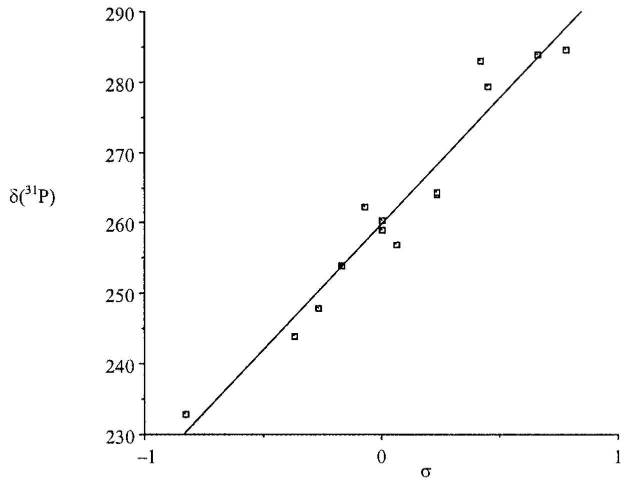


Figure 4. Hammett plot for values of $\delta(^{31}P)$ of **6**

$$\delta(^{31}P) = 259.81 + 35.62\sigma_p \ (R = 0.941) \tag{7}$$

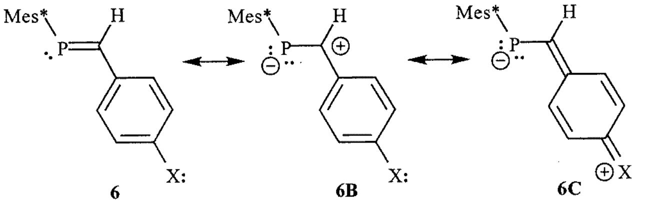
$$\delta(^{31}P) = 264.26 + 21.98\sigma_p^{+} \ (R = 0.934) \tag{8}$$

$$\delta(^{31}P) = 253.33 + 46.29\sigma^{n} \ (R = 0.888) \tag{9}$$

Nevertheless, a more detailed analysis of the data for Equation (9) reveals particularly pronounced deviations for compounds **6a−d** with the strongly electron-donating substituents X = NMe_2, OH, OMe, and Me; this observation may be considered as an indication that the purely inductive constant σ^n is inadequate in these cases. With appropriate caution, in view of the limited number of data points (four), we derived Equation (10) with σ_p^{+} for these compounds and obtained a particularly good correlation ($R = 0.992$)!

$$\delta(^{31}P) = 258.91 + 15.26\sigma_p^{+} \ (R = 0.992) \tag{10}$$

This result might be taken as evidence for a resonance interaction that is stronger than normal, as expressed by structures **6B** (Scheme 6, corresponding to **1B** of Scheme 1) and **6C**. For obvious reasons, **6C** is not relevant in the case of electron-withdrawing substituents X. Such an exceptional effect is plausible if one assumes that in **6**, the value of $\delta(^{31}P)$ is particularly sensitive to perturbations of the π system, which also has been suggested[29,30] to be a major factor responsible for the normally good correlation between values of $\delta(^{13}C)$ and σ_p^{+}.



Scheme 6

One may conclude that, in general, the interaction between the P=C bond and the aromatic system is dominated by inductive effects while resonance effects play a minor role only, unless a very specific π interaction occurs, as evidenced by the value of $\delta(^{31}P)$, which may, however, be compensated in part in the σ system.[34,35]

Conclusion

The linear free-energy relationships, derived for the phosphaalkenes **6** from the values of pK_a of substituted benzoic acids and from the values of $\delta(^{13}C_{para})$ of substituted benzoic acids **7** and bromobenzenes **8**, indicate that the (*E*)-Mes*P=CH group is a weak electron donor with mainly an inductive effect on a neighboring benzene ring; resonance structures such as **1A** and **1B** are normally of minor importance. In this regard, it is surprisingly analogous to the C=C bond, and this result confirms the well-known diagonal relationship in the Periodic System, justifying the slogan "Phosphorus: The Carbon Copy".[4]

Experimental Section

General Remarks: All experiments were performed under N_2 in glassware that had been oven-dried at 150 °C. Solid starting materials were dried under vacuum; liquid starting materials were distilled under N_2. Solvents were distilled from $LiAlH_4$ (pentane, diethyl ether) or from sodium/benzophenone (THF). NMR spectra were obtained at room temperature with a Bruker WM 250 spectrometer (^{31}P: 101.25 MHz) or with a Bruker AC 200 spectrometer (^{13}C: 50.32 MHz; ^{1}H: 200.13 MHz). High-resolution mass spectra (HRMS) were obtained with a Finnigan MAT 5 spectrometer. Elemental analyses were performed by Microanalytisches Labor Pascher, Remagen, Germany. Benzoic acids **7** and bromobenzenes **8** were available from commercial sources. Measurements of the value of pK_a were performed with a Mettler DL25 Titrator by titrating a solution of the benzoic acid (**6l**, **7**) in 85.6% ethanol/water with 0.1005 N aqueous NaOH.

[(*E*)-4-Bromobenzylidene](2,4,6-tri-*tert*-butylphenyl)phosphane (6j): Under vigorous stirring at −65 °C, a solution of *n*-butyllithium (1.6 M in hexane, 15.7 mL, 25 mmol) was added to a solution of Mes^*PH_2[36] (6.9 g, 25 mmol) in THF (100 mL). After 5 min, the solution was warmed to room temperature and stirred for another 15 min. To the red-brown reaction mixture, *tert*-butyldimethylsilyl chloride (3.75 g, 25 mmol) was added, followed by stirring for 30 min. *n*-Butyllithium (1.6 M in hexane, 15.7 mL, 25 mmol) was added to the orange reaction mixture. After 15 min, the reaction mixture was cooled to −65 °C and *p*-bromobenzaldehyde (4.61 g, 25 mmol) was added, followed by warming to room temperature and stirring for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in pentane (100 mL). Trimethylsilyl chloride (3.22 mL, 25 mmol) was added to the resulting solution. After stirring for 30 min, the yellow suspension was filtered through Al_2O_3 and the filtrate was concentrated to dryness to yield practically pure **6j** as a yellow powder (10.37 g, 23.3 mmol, 93%); light-yellow crystals (8.41 g, 18.9 mmol, 76%) were obtained after recrystallization from acetonitrile. M.p. 136−137 °C (no m.p. reported in the literature[22]). ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 9 H, *p-t*Bu), 1.44 (s, 18 H, *o-t*Bu), 7.35−7.38 (m, 6 H, Ar-*H*), 7.96 (d, $^2J_{P,H}$ = 25.4 Hz, 1 H, vinyl-*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 31.4 [s, *p*-C(*C*H$_3$)$_3$], 33.8 [d, $^4J_{P,C}$ = 7.0 Hz, *o*-C(*C*H$_3$)$_3$], 35.0 [s, *p*-*C*(CH$_3$)$_3$], 38.2 [s, *o*-*C*(CH$_3$)$_3$], 121.6 [d, $^5J_{P,C}$ = 9.3 Hz, *p*-C$_6$H$_4$(*C*)], 121.8 [s, *m*-Ar(*C*)], 127.1 [d, $^3J_{P,C}$ = 22.1 Hz, *o*-C$_6$H$_4$(*C*)], 131.8 [d, $^4J_{P,C}$ = 3.0 Hz, *m*-C$_6$H$_4$(*C*)], 138.5 [d, $^1J_{P,C}$ = 53.3 Hz, *i*-Ar(*C*)], 138.9 [d, $^2J_{P,C}$ = 14.1 Hz, *i*-C$_6$H$_4$(*C*)], 149.8 [s, *p*-Ar(*C*)], 154.0 [s, *o*-Ar(*C*)], 174.4 (d, $^1J_{P,C}$ = 34.6 Hz, P=*C*) ppm. ^{31}P NMR ($CDCl_3$): δ = 264.4 ppm. $C_{25}H_{34}{}^{79}BrP$: calcd. 444.1582, found (HRMS EI) 444.1585.

[(*E*)-4-Cyanobenzylidene](2,4,6-tri-*tert*-butylphenyl)phosphane (6n): According to the procedure described for **6j**, Mes*PH$_2$ (1.1 g, 4 mmol) was converted into **6n** by reaction with *p*-cyanobenzaldehyde (0.52 g, 4 mmol) to give a light-yellow powder of **6n** (1.49 g, 3.81 mmol, 95%); light-yellow needles (1.14 g; 2.92 mmol; 73%) were obtained after recrystallization from acetonitrile. M.p. 98−101 °C. ^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 9 H, *p-t*Bu), 1.52 (s, 18 H, *o-t*Bu), 7.47−7.62 (m, 6 H, Ar-*H*), 8.07 (d, $^2J_{P,H}$ = 25.1 Hz, 1 H, vinyl-*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 31.2 [s, *p*-C(*C*H$_3$)$_3$], 33.8 [d, $^4J_{P,C}$ = 6.9 Hz, *o*-C(*C*H$_3$)$_3$], 34.9 [s, *p*-*C*(CH$_3$)$_3$], 38.1 [s, *o*-*C*(CH$_3$)$_3$], 110.4 [d, $^5J_{P,C}$ = 8.2 Hz, *p*-C$_6$H$_4$(*C*)], 119.1 (s, *C*N), 121.9 [s, *m*-Ar(*C*)], 125.9 [d, $^3J_{P,C}$ = 22.4 Hz, *o*-C$_6$H$_4$(*C*)], 132.4 [d, $^4J_{P,C}$ = 3.0 Hz, *m*-C$_6$H$_4$(*C*)], 137.6 [d, $^1J_{P,C}$ = 53.1 Hz, *i*-Ar(*C*)], 144.0 [d, $^2J_{P,C}$ = 14.6 Hz, *i*-C$_6$H$_4$(*C*)], 150.1 [s, *p*-Ar(*C*)], 153.9 [d, $^2J_{P,C}$ = 1.5 Hz, *o*-C$_6$H$_4$(*C*)], 172.5 (d, $^1J_{P,C}$ = 36.0 Hz, P=*C*) ppm. ^{31}P NMR ($CDCl_3$): δ = 283.9 ppm. $C_{26}H_{34}NP$: calcd. 391.2429, found (HRMS EI) 391.2428. $C_{26}H_{34}NP$ (391.51): calcd. C 79.75, H 8.76; found C 79.78, H 8.77.

(2,4,6-Tri-*tert*-butylphenyl)[(*E*)-4-(trimethylsilyl)benzylidene]phosphane (6e): Under vigorous stirring at −65 °C, *n*-butyllithium in hexane (1.6 M in hexane, 1.98 mL, 3.0 mmol) was added to a solution of **6j** (1.32 g, 3.0 mmol) in THF (20 mL). After 5 min, trimethylsilyl chloride (0.36 mL, 3.0 mmol) was added. The reaction mixture was warmed to room temperature and then concentrated to dryness under vacuum. The residue was extracted with pentane; the extract was dried ($MgSO_4$), filtered, and the solvents were evaporated to dryness. The light-yellow residue (1.26 g, 96%) was recrystallized from acetonitrile to yield **6e** as light-greenish needles (1.05 g, 80%). M.p. 181−183 °C. ^{1}H NMR ($CDCl_3$): δ = 0.30 [s, 9 H, Si(C*H*$_3$)$_3$], 1.39 (s, 9 H, *p-t*Bu), 1.55 (s, 18 H, *o-t*Bu), 7.48−7.62 (m, 6 H, Aryl-*H*), 8.17 (d, $^2J_{P,H}$ = 25.5 Hz, 1 H, vinyl-*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = −1.2 [s, Si(*C*H$_3$)$_3$], 31.4 [s, *p*-C(*C*H$_3$)$_3$], 33.8 [d, $^4J_{P,C}$ = 7.0 Hz, *o*-C(*C*H$_3$)$_3$], 34.9 [s, *p*-*C*(CH$_3$)$_3$], 38.2 [s, *o*-*C*(CH$_3$)$_3$], 121.7 [s, *m*-Ar(*C*)], 124.9 [d, $^3J_{P,C}$ = 21.9 Hz, *o*-C$_6$H$_4$(*C*)], 133.7 [d, $^4J_{P,C}$ = 2.7 Hz, *m*-C$_6$H$_4$(*C*)], 139.0 [d, $^1J_{P,C}$ = 53.6 Hz, *i*-Ar(*C*)], 140.4 [s, *p*-C$_6$H$_4$(*C*)], 140.4 [d, $^2J_{P,C}$ = 13.9 Hz, *i*-C$_6$H$_4$(*C*)], 149.6 [s, *p*-Ar(*C*)], 154.0 [s, *o*-Ar(*C*)], 175.6 (d, $^1J_{P,C}$ = 34.8 Hz, P=*C*) ppm. ^{31}P NMR ($CDCl_3$): δ = 262.3 ppm. $C_{28}H_{43}P^{28}Si$: calcd. 438.2872, found (HRMS EI) 438.2872. $C_{28}H_{43}PSi$ (438.68): calcd. C 76.65, H 9.89; found C 76.79, H 9.85.

(2,4,6-Tri-*tert*-butylphenyl)[(*E*)-4-(trimethylstannyl)benzylidene]phosphane (6g): Under vigorous stirring at −65 °C, *n*-butyllithium in hexane (1.6 M in hexane, 2.60 mL, 4.0 mmol) was added to a solution of **6j** (1.78 g, 4.0 mmol) in THF (25 mL). After 5 min, trimethyltin chloride (1.0 g, 5 mmol) was added. The reaction mixture was warmed to room temperature and then concentrated to dryness under vacuum. The residue was extracted with pentane; the extract was dried ($MgSO_4$), filtered, and the solvents were evaporated to dryness. The light-yellow residue (2.10 g, 99%) was recrystallized from acetonitrile to yield **6g** as a white powder (1.78 g, 84%). M.p. 140−142 °C. ^{1}H NMR ($CDCl_3$): δ = 0.46 [s, 9 H, Sn(C*H*$_3$)$_3$], 1.53 (s, 9 H, *p-t*Bu), 1.69 (s, 18 H, *o-t*Bu), 7.60−7.73 (m, 6 H, Ar-*H*), 8.30 (d, $^2J_{P,H}$ = 25.4 Hz, 1 H, vinyl-*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = −9.6 [s, Sn(*C*H$_3$)$_3$], 31.4 [s, *p*-C(*C*H$_3$)$_3$], 33.8 [d, $^4J_{P,C}$ = 7.0 Hz, *o*-C(*C*H$_3$)$_3$], 34.9 [s, *p*-*C*(CH$_3$)$_3$], 38.2 [s, *o*-*C*(CH$_3$)$_3$], 121.7 [s, *m*-Ar(*C*)], 125.2 [d, $^3J_{P,C}$ = 22.0 Hz, *o*-C$_6$H$_4$(*C*)], 136.2 [d, $^4J_{P,C}$ = 2.6 Hz, *m*-C$_6$H$_4$(*C*)], 139.0 [d, $^1J_{P,C}$ = 53.7 Hz, *i*-Ar(*C*)], 140.0 [d, $^2J_{P,C}$ = 13.8 Hz, *i*-C$_6$H$_4$(*C*)], 142.7 [s, *p*-C$_6$H$_4$(*C*)], 149.6 [s, *p*-Ar(*C*)], 154.0 [s, *o*-Ar(*C*)], 175.8 (d, $^1J_{P,C}$ = 34.6 Hz, P=*C*) ppm. ^{31}P NMR ($CDCl_3$): δ = 260.7 ppm. $C_{28}H_{43}P^{116}Sn$ calcd. 526.2123, found (HRMS EI) 526.2126. $C_{28}H_{43}PSn$ (529.30): calcd. C 63.53, H 8.19; found C 64.82, H 8.30.

4-{[(*E*)-(2,4,6-Tri-*tert*-butylphenyl)phosphanylidene]methyl}benzaldehyde (6k): Under vigorous stirring at −65 °C, *n*-butyllithium in hexane (1.6 M in hexane, 2.60 mL, 4.0 mmol) was added to a solution of **6j** (1.78 g, 4.0 mmol) in THF (25 mL). After 5 min, *N*,*N*-dimethylformamide (0.31 mL, 4 mmol) was added to the dark-orange reaction mixture. The reaction mixture turned green and was warmed to room temperature. After quenching with aqueous NH_4Cl, the solvents were evaporated to dryness under vacuum. The yellow residue was extracted with pentane (25 mL); the extract was dried ($MgSO_4$), filtered, and the solvents were evaporated to dryness. The light-yellow residue (1.47 g, 93%) was recrystallized from acetonitrile to yield **6k** as yellow needles (1.30 g, 82%). M.p. 125−127 °C. ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 9 H, *p-t*Bu), 1.43 (s, 18 H, *o-t*Bu), 7.16−7.75 (m, 6 H, Ar-*H*), 8.25 (d, $^2J_{P,H}$ = 25.1 Hz, 1 H, vinyl-*H*), 9.88 (s, 1H C*H*O) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 31.2 [s, *p*-C(*C*H$_3$)$_3$], 33.7 [d, $^4J_{P,C}$ = 7.0 Hz, *o*-C(*C*H$_3$)$_3$], 34.9 [s, *p*-*C*(CH$_3$)$_3$], 38.1 [s, *o*-*C*(CH$_3$)$_3$], 121.9 [s, *m*-Ar(*C*)], 126.0 [d, $^3J_{P,C}$ = 22.4 Hz, *o*-C$_6$H$_4$(*C*)], 130.2 [d, $^4J_{P,C}$ = 2.9 Hz, *m*-C$_6$H$_4$(*C*)], 135.2 [d, $^5J_{P,C}$ = 7.1 Hz, *p*-C$_6$H$_4$(*C*)], 138.0 [d, $^1J_{P,C}$ = 53.4 Hz, *i*-Ar(*C*)], 145.7 [d, $^2J_{P,C}$ = 14.0 Hz, *i*-C$_6$H$_4$(*C*)], 150.0 [s, *p*-Ar(*C*)], 153.9 [s, *o*-Ar(*C*)], 173.3 (d, $^1J_{P,C}$ = 36.0 Hz, P=*C*), 191.4 (s, *C*HO) ppm. ^{31}P NMR ($CDCl_3$): δ = 283.1 ppm. $C_{26}H_{35}OP$: calcd. 394.2426, found (HRMS EI) 394.2427. $C_{26}H_{35}OP$ (394.51): calcd. C 79.15, H 8.95; found C 79.31, H 8.89.

4-{[(*E*)-(2,4,6-Tri-*tert*-butylphenyl)phosphanilidene]methyl}benzoic Acid (6l): Under vigorous stirring at −65 °C, *n*-butyllithium in hexane (1.6 M in hexane, 2.60 mL, 4.0 mmol) was added to a solution of **6j** (1.78 g, 4.0 mmol) in THF (25 mL). After 5 min, an excess of CO_2 was sublimed into the dark-orange reaction mixture, which was then stirred for another 5 min and warmed to room temperature. Trimethylsilyl chloride (1.2 mL, 9.5 mmol) was added to the resulting yellow suspension; the precipitate dissolved, water (0.5 mL, 28 mmol) was added, and the mixture was concentrated to dryness under vacuum. The residue was extracted with $CHCl_3$ (20 mL); the extract was washed with water, dried ($MgSO_4$), filtered, and then the solvents were evaporated to dryness. The yellow residue (1.59 g, 97%) was recrystallized from acetonitrile to yield **6l** as yellow needles (1.09 g, 66%). M.p. 215−217 °C. ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 9 H, *p-t*Bu), 1.44 (s, 18 H, *o-t*Bu), 7.38 (s, 2 H, Ar-*H*), 7.56 (dd, $^3J_{H,H}$ = 8.1, $^4J_{P,H}$ = 3.1 Hz, 2 H, *o*-C$_6$H$_4$-*H*), 7.97 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2 H, *m*-C_6H_4-*H*), 8.10 (d, $^{2}J_{P,H}$ = 23.5 Hz, 1 H, vinyl-*H*), 11.97 (br. s, 1 H, COO*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 31.2 [s, *p*-C(CH_3)$_3$], 33.7 [d, $^{4}J_{P,C}$ = 6.9 Hz, *o*-C(CH_3)$_3$], 34.9 [s, *p*-*C*(CH_3)$_3$], 38.1 [s, *o*-*C*(CH_3)$_3$], 121.8 [s, *m*-Ar(*C*)], 125.4 [d, $^{3}J_{P,C}$ = 22.0 Hz, *o*-C_6H_4(*C*)], 127.9 [d, $^{5}J_{P,C}$ = 7.3 Hz, *p*-C_6H_4(*C*)], 130.6 [d, $^{4}J_{P,C}$ = 2.4 Hz, *m*-C_6H_4(*C*)], 138.3 [d, $^{1}J_{P,C}$ = 53.4 Hz, *i*-Ar(*C*)], 145.0 [d, $^{2}J_{P,C}$ = 14.0 Hz, *i*-C_6H_4(*C*)], 149.9 [s, *p*-Ar(*C*)], 153.9 [s, *o*-Ar(*C*)], 171.8 (s, *C*OOH), 173.5 (d, $^{1}J_{P,C}$ = 35.7 Hz, P=*C*) ppm. ^{31}P NMR ($CDCl_3$): δ = 279.4 ppm. $C_{26}H_{35}O_2P$: calcd. 410.2375, found (HRMS EI) 410.2376. $C_{26}H_{35}O_2P$ (410.51): calcd. C 76.06, H 8.60; found C 76.30, H 8.78.

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