Synthesis and Characterization of β-Phosphaenones An Investigation on the Conjugative Properties of the P=C Bond

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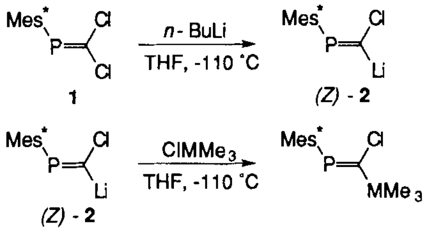
Thermally and air-stable β-phosphaenones were synthesized by functionalization of Mes*P=CCl_2 (**1**; Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl). At low temperature, **1** was lithiated by halogen-metal exchange with *n*-butyllithium to give the phosphanylidene carbenoid (Z)-Mes*P=C(Cl)Li [(Z)-**2**] which reacted with acid chlorides to furnish the C-carbonyl-substituted phosphaalkenes (Z)-Mes*P=C(Cl)R (**3**: R = CO*t*Bu; **4**: R = COPh; **5**: R = COOEt). The reaction of (Z)-**2** with carbon dioxide furnished the carboxylate **6**, which was converted by treatment with pivaloyl chloride or trimethylsilyl chloride into the phosphaalkenes **7** and **8** functionalized at the carbon atom by an anhydride or a trimethylsilyl ester function, respectively. Acidification of **6** or hydrolysis of **8** with water in chloroform solution afforded the novel carboxylic acid (Z)-Mes*P=C(Cl)COOH (**9**). Spectroscopic investigations (NMR, UV, IR) of **3**–**9** and the X-ray structures of **3** and **4** are presented. Based on these properties and on theoretical calculations, the occurrence of conjugation in the β-phosphaenone system is discussed and compared with the well-known conjugation in normal enones.

Introduction

During the past decade, considerable progress has been made in the synthesis of phosphaalkenes bearing halogen atoms at the carbon atom (Mes*-P=CX_2; X = Cl, Br, I; Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl)[1–5]. Interest in this class of compounds stems in part from their potential as key synthons for the preparation of new functionalized phosphaalkenes, for instance by transformation to phosphanylidene carbenoids which can function as nucleophilic organometallic species[2b,2c,5a,5b]. A relevant example is the halogen-metal exchange between *n*-butyllithium and dichloromethylene-(2,4,6-tri-*tert*-butylphenyl)-phosphane (**1**) which gives the phosphanylidene carbenoid (*Z*)-**2** in high yield (Scheme 1)[2b,5a].

An adventitious circumstance of this reaction is its stereoselectivity. Presumably due to the steric hindrance by the supermesitylene (Mes*) group, only the (*E*)-chlorine is exchanged with formation of (*Z*)-**2**. Carbenoid (*Z*)-**2** is thermally unstable and rearranges at about −50°C with formation of the phosphaacetylene Mes*C≡P[5c]. However, at low temperature, it is thermally and configurationally stable, and it reacts stereospecifically with proton donors and other electrophiles to yield the *trans*-substituted products. Only a limited number of reactions of this type are known, including those with methanol[2b], methyl iodide[2b,5b] and chlorotrimethyl derivatives of group 14[2b,2c,5a] as electrophilic reagents. The latter reaction is shown in Scheme 1.

Scheme 1



So far, only few phosphaenones have been reported; they were synthesized from appropriate saturated precursors by elimination of HCl with formation of the phosphaalkene double bond. Unfortunately, those phosphaenones were thermally unstable or polymerized on mild heating[6]. In this paper, we report on the synthesis and characterization of thermally stable phosphaenones and carboxylic acid derivatives accessible from **1** via the reaction of (*Z*)-**2** with acid chlorides or carbon dioxide. The availability of thermally stable phosphaenones enabled us to investigate the spectroscopic and structural properties of this class of compounds.

Synthesis of β-Phosphaenones

As reported previously[2b,2c,5a,5b], the reaction of *n*-butyllithium with **1** at −110°C quantitatively gives (*Z*)-**2**. At the same temperature, pivaloyl chloride, benzoyl chloride, or ethyl chloroformate were added, respectively, and the reac-

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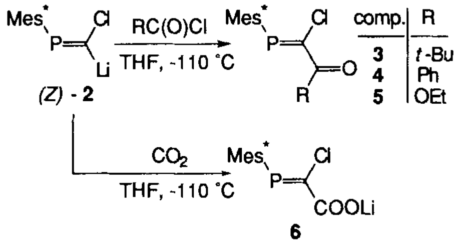
tion mixtures were warmed to room temperature within one hour. Compounds **3** (83%), **4** (88%), and **5** (86%), respectively, were isolated as air-stable crystalline compounds (Scheme 2).

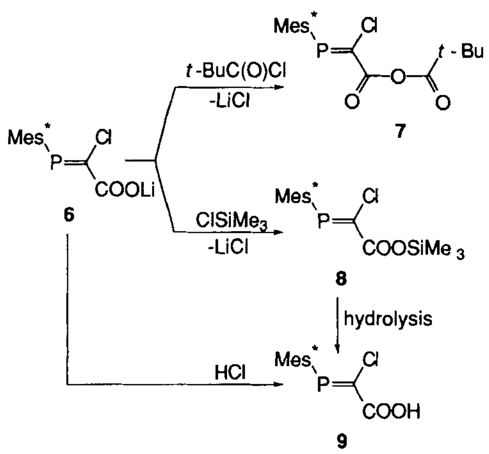
When carbon dioxide was sublimed into the reaction mixture containing **2**, the novel β-phosphaacrylate anion **6** [δ(^{31}P, [D$_8$]THF) = 282] was formed. Surprisingly, this anion is very stable, even at elevated temperatures; it survives refluxing its THF solution for two hours without decomposition or polymerization (Scheme 2).

Scheme 2



Carboxylate **6** could be isolated by concentration of the THF solution (addition of water or a saturated solution of ammonium chloride in water to **6** in THF furnished a transparent gel; its formation was not further investigated). Evaporation of the volatile products from the original reaction mixture gave a white solid which was characterized to be **6**. Carboxylate **6** was further characterized by derivatization. Addition of pivaloyl chloride to the crude reaction mixture containing **6** furnished an anhydride **7** [δ(^{31}P, C_6D_6) = 340] as the only product (Scheme 3). Addition of trimethylsilyl chloride gave the silyl ester **8** [δ(^{31}P, C_6D_6) = 318] as the only product. After work-up, **7** and **8** were isolated in 76% and 82% yield, respectively. Addition of water and chloroform to **6** produced a "milky" emulsion. Acidification of this emulsion with HCl led to phase separation, yielding a chloroform layer, which contained the carboxylic acid derivative **9** [δ(^{31}P, $CDCl_3$) = 332], and an aqueous layer (pH = 1). Concentration of the chloroform layer gave **9** in 85% yield. Hydrolysis of **8** with water in chloroform solution also produced **9** in 100% yield.

Scheme 3



Spectroscopic Investigation of 3−9

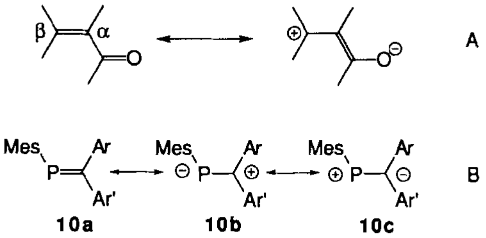
General Considerations

One of the most intriguing aspects of β-phosphaenones is their structural analogy to normal enones. In this context the question arises if, or to what extent, the P=C unit in P=C−C=O is comparable to the C=C unit in C=C−C=O, in particular with respect to their conjugative ability.

An important feature of enones is the conjugation between the C=C and C=O group, which is optimal when the system is planar (Scheme 4A)[7]. As a result, π-electron density is transferred from the C=C bond, especially from the β-carbon to the carbonyl oxygen. However, this π-delocalization does not affect overall charge distributions, since σ-electrons tend to counteract any movement by π-electrons[8a,b]. Nevertheless, commonly used indicators of conjugation are the ^{13}C-NMR data and the C=C, C=O and C−C bond lengths (vide infra). In conjugated enones, the ^{13}C-β signal is deshielded (Δδ = +5 to +15) and the ^{13}C(C=O) signal is shielded (Δδ = −2 to −20) with respect to the analogous function in nonconjugated model compounds (Δδ values were derived from collections of ^{13}C data)[7,9].

A priori, our expectations on how the P=C bond would behave in conjugation with the carbonyl group were mixed because the polarization of the P=C bond is a rather complicated matter. Previous investigations have shown that, towards (substituted) phenyl rings at the olefinic carbon atom, phosphaalkenes act as electron-withdrawing substituents (the Hammet σ values of P=C−Ar were found to be 0.2 to 0.3), as presented by formula **10b** (Scheme 4B)[10].

Scheme 4



The stronger electron-withdrawing character of phosphorus with respect to carbon was confirmed by investigation of compound **9**. Determination of the pK_a of benzoic acid, acrylic acid and **9** in 85.6 wt-% ethanol/water medium revealed an acidity order of **9**: (5.8) > acrylic acid: (6.8) > benzoic acid: (7.0). With the reservation that in this comparison the effect of the α-chloro substituent in **9** is neglected, this relative acidity order indicates the stronger anion-stabilizing effect of the P=C unit as compared to the C=C unit.

This is contrary to intuition, as phosphorus is more electropositive than carbon, and indeed, X in HX (X = Cl, Br, I) adds to phosphorus as if resonance structure **10c** would be predominant[11]. Thus, the two pieces of experimental evidence seem, at first glance, to be contradictory, but they can be reconciled as follows: One may assume with some confidence that structure **10b** is indeed preferred to **10c**, because in the latter, phosphorus is in a dicoordinate, positively charged, "cationic state", which is highly unfavorable. On the other hand, **10b** is representative of the π-system only, and the natural charge distribution $^{\delta+}P-C^{\delta-}$ may be restored via the σ-system as demonstrated by calculations of Wiberg et al. in the case of acrolein[8]. Waluk et al. have concluded that in π-orbital systems phosphorus is indeed slightly more electronegative than carbon[12]. Note, however, that this direction of polarization of the P=C π-system (cf. **10b**) is highly unfavorable for phosphaenones, as its positively charged carbon is adjacent to the strongly electron-withdrawing carbonyl group.

The extent of conjugation was also difficult to predict. Nyulászi et al. have concluded from calculations of the π-ionization energy that the conjugative behavior of the P=C π-system is comparable to that of the C=C π-system, although the π-component of the P=C bond is only 58% as strong as that of the C=C bond[13]. Taking all these facts into account, it seemed a risky enterprise to predict the behaviour of the P=C bond in our β-phosphaenone systems.

NMR Spectra

First, we will compare the NMR data of **3**–**9** with those of non-conjugated phosphaalkenes (Table 1). ^{31}P-NMR measurements (C_6D_6) show deshielding of the phosphorus nucleus compared to (*Z*)-chloromethylene-(2,4,6-tri-*tert*-butylphenyl)phosphane [(*Z*)-Mes*P=C(Cl)H; $\delta(^{31}P)$ = 249][2c]. The changes vary from +43 ppm for **3** to +91 ppm for **7** and are, qualitatively, as expected for conjugation of the phosphaalkene with the carbonyl group, in a manner analogous to that of its carbon analogues (cf. Scheme 4A).

Table 1. NMR data of phosphaenones **3**–**9**[a]

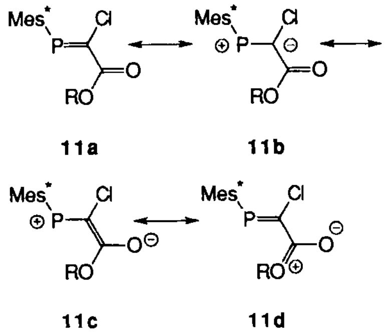
	$\delta(^{31}P)$			$\delta(^{13}C)$		
Compound	C_6D_6	$CDCl_3$	$\Delta\delta$[b]	(P=C)	(C=O)	^1J(PC)[c]
(*Z*)-Mes*P=CHCl	249	249	0	149	--	59
3	292	303	11	164	201	69
4	321	334	13	167	190	71
5	311	315	4	156	164	67
6	282[d]	--	--	171	168	62
7	340	343	3	155	173	69
8	318	321	3	159	164	68
9	--	332	--	153[e]	169[e]	69[e]

[a] Measurements in C_6D_6 unless otherwise stated. – [b] $\Delta\delta = \delta(CDCl_3) - \delta(C_6D_6)$. – [c] In Hz. – [d] In [D_8]THF. – [e] In $CDCl_3$.

When changing the solvent from benzene to chloroform, additional deshielding was observed for **3** (+11 ppm) and **4** (+13 ppm). For **5**, **7**, and **8**, the amount of deshielding was limited to +3 to +4 ppm. The more pronounced dependence of $\delta(^{31}P)$ of **3** and **4** on solvent polarity may reflect a stronger polarization of these compounds as compared to **5**, **7**, and **8**. In the latter three, the electron-withdrawing power of the carbonyl group, as illustrated by resonance structure **11c**, is apparently tempered by contributions from structure **11d** (Scheme 5). For **5** and **8** this is in line with expectation in view of the general behavior of ester functionalities. For **7** it was unexpected because, in general, the carbonyl group of an anhydride is assumed to display a stronger electron-withdrawing effect than a normal keto carbonyl group, and indeed, its phosphorus nucleus is the most deshielded one of the series.

The phosphaalkene carbon in **3**–**9** is not shielded, as might be expected for the resonance structure **11b**. Rather, it is deshielded relative to (*Z*)-Mes*P=CHCl, possibly indicating electron release from the P=C unit to the carbonyl group as in **11c**.

Scheme 5



Incidentally, the chemical shifts of the two nuclei of the P=C moiety show an interesting trend which is also reflected in the ^{13}C-NMR data of substituted alkenes [CH_2=CHR; R = C(=O)R′, halogen, aliphatic carbon]. It may be called a "compensation effect". This empirical, qualitative effect correlates the shielding of C-α with the deshielding of C-β (for comparable substituents R) such that the values of $(\delta^{13}C_\alpha + \delta^{13}C_\beta)/2$ are nearly constant and fall into a characteristic range depending on the electronic nature of R. For example, aliphatically substituted ethenes show an average value of approximately 125 ppm[14]. For R = C(=O)R′ the characteristic value is 133 ppm, indicating an overall release of electron density from the alkene to the carbonyl group[14]. An analogous rule applies to phosphaalkenes and β-phosphaenones. Phosphaalkenes show an average $(\delta^{13}C_\alpha + \delta^{13}P_\beta)/2$ value of approximately 200 ppm[15], while that of phosphaenones is about 237 ppm, again indicating electron withdrawal by the carbonyl group.

^{13}C (C=O)-NMR chemical shifts of the phosphaenones are shielded ($\Delta\delta = -2$ to -20) compared to those of non-conjugated carbonyl compounds, which is analogous to enone behavior[7,9]. This can be understood by taking into account the contribution of structures like **11c** (Scheme 5).

Infrared Spectra

Infrared spectra (KBr) of phosphaenones show carbonyl stretching frequencies in the conjugated region. Conjugation goes along with weakening of the C=O bond and results in a red shift of the C=O frequencies. This effect of the phosphaalkenes on the carbonyl frequencies is analogous to that of normal olefins on the C=O stretching frequencies in enones. In the α,β-unsaturated series, the IR frequencies range for ketones from 1695 to 1675 cm^{-1}, for esters from 1720 to 1705 cm^{-1}, and for anhydrides from 1760 to 1710 cm^{-1}. The values of the phosphaenones roughly fit into these ranges (Table 2). Although a direct correlation between the ^{31}P chemical shifts and the C=O frequencies may not be expected, one observes that deshielding of the phosphorus nucleus goes along with a weakening of the C=O bond, as if the weight of resonance structure $^{\delta+}$P−C=C−O$^{\delta-}$ increases (for a detailed analysis, see Discussion).

Table 2. Carbonyl stretching frequencies and n-π* transitions of **1**, **3**–**9**

Compound	ν (cm^{-1})[a]	λ_{max} (lg ε)[b]
1	--	274 (4.007)
3	1643	300 (3.849)
4	1649	305 (4.042)
5	1712	293 (3.988)
6	1614, 1363	290 (3.912)
7	1720, 1784	-- [c]
8	1695	-- [c]
9	1691	290 (3.822)

[a] In KBr. – [b] In EtOH. – [c] Not determined.

UV Spectra

UV measurements show the n-π*(P=C) transition of the phosphaenones as the only accessible absorption maximum. The yellow color of phosphaenones **3** and **4** arises from tailing of the n-π* transition into the visible region (Table 2). Compound **5** is only slightly colored, and **9** is a slightly yellowish solid. Conjugation of the phosphaalkene decreases the n-π* energy gap, and thus the n-π* absorptions of the phosphaenones are found at higher wavelengths (λ_{max} = 290–305 nm) than those of nonconjugated phosphaalkenes (e.g. Mes*P=CCl$_2$: λ_{max} = 274 nm, lg ε = 4.007[16]). This bathochromic shift of the n-π* transitions due to conjugation is in line with the bathochromic shift of the π-π* transitions of conjugated olefins. Again, only a qualitative correlation between deshielding of the phosphorus nuclei and a red shift in the UV spectrum is observed. However, carboxylic acid derivatives of olefins show a hypsochromic shift compared to the corresponding aldehydes. This effect is also observed in the phosphaenones; the RO substituents at the carbonyl moiety of **5** and **9** apparently reduce conjugation, and thus cause a relative blue shift of the n-π* transitions.

X-Ray Crystal Structure Analysis of 3 and 4

Bond lengths and conformations were expected to give additional information on whether or not conjugation is present in phosphaenones. Compounds **3** and **4** were crystallized from pentane yielding single crystals suitable for X-ray structure determination (Figures 1, 2; Table 3, 4).

The most surprising aspect of the structures of **3** and **4** is the generally normal value of the bond lengths in the P=C−C=O partial structure. Clear-cut evidence for the effects of conjugation is missing. The P=C−C=O moiety of **3** is planar (torsion angle = 0°) and has the s-*cis* conformation, whereas in **4**, it has the s-*trans* conformation with a torsion angle of 162.57(19)°. The phenyl group of **4** is rotated out of the P−C−C−O plane [torsion angle C(10)−C(9)−C(8)−O(1): 134.6(2)°] and therefore only partially involved in conjugation with the enone π-system. The C(1)−P−C(2) angles in **3** [102.38(19)°] and **4** [103.57(11)°] are not significantly different from that of **1** [102.63(15)°][16]. The Cl(1)−C(1)−C(14) angle in **3** [118.9(3)°] is larger than the Cl(1)−C(1)−C(8) angle in **4** [113.47(16)°] and the Cl(1)−C(1)−Cl(2) angle in **1** [112.86(19)°]. This is probably a consequence of steric interactions.

Figure 1. Thermal motion ellipsoid plot (30% probability level) of $C_{24}H_{38}ClOP$ (**3**)[30]. Hydrogen atoms are omitted for clarity

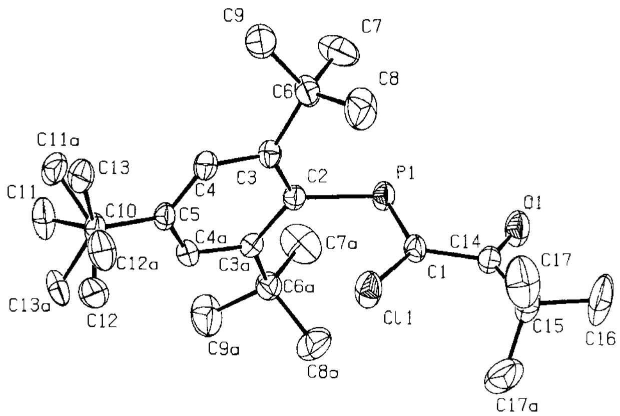
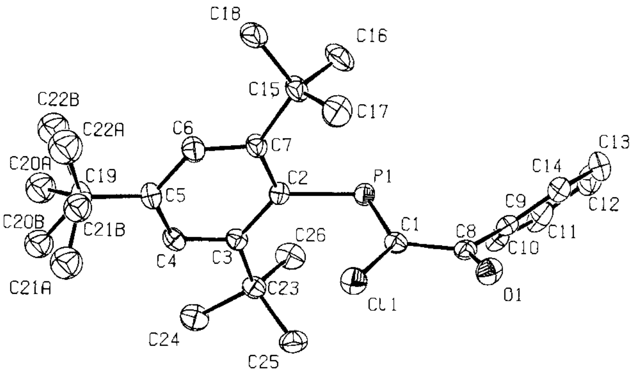


Figure 2. Thermal motion ellipsoid plot (50% probability level) of $C_{26}H_{34}ClOP$ (**4**)[30]. Hydrogen atoms are omitted for clarity



In conjugated enones the C=O and C=C bonds are expected to be longer, and the C−C bond to be shorter, than in nonconjugated systems (Scheme 4A). Indicative of possible conjugation in **3** and **4** are the C=O, C−C, and P=C bond lengths. As stated above, the general structural parameters do not signal typical conjugation effects. First, the C=O bond of **3** [1.207(6) Å] is even shorter (Δ*d* = 0.012 Å) than the average bond of aliphatically substituted enones (1.219 Å)[7b]. The C=O bond length of **4** [1.217(3) Å] is (slightly) shorter (Δ*d* = 0.007 Å) than the average value of

Table 3. Crystallographic data for **3** and **4**

Complex	**3**	**4**
Crystal data		
Formula	$C_{24}H_{38}ClOP$	$C_{26}H_{34}ClOP$
Molecular weight	408.99	428.98
Crystal system	monoclinic	triclinic
Space group	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)
a, Å	9.631(2)	9.9336(10)
b, Å	12.185(2)	10.5900(10)
c, Å	10.349(3)	12.0261(10)
α, deg	90	109.413(10)
β, deg	92.70(2)	89.868(10)
γ, deg	90	95.139(10)
V,Å^3	1213.1(5)	1187.9(2)
D_{calc}, g cm^{-3}	1.120	1.199
Z	2	2
$F(000)$	444	460
μ, cm^{-1}	2.3	2.4
Crystal size, mm	0.40 x 0.40 x 0.40	0.50 x 0.55 x 0.35
Data collection		
T, K	298	150
$\theta_{min}, \theta_{max}$ deg	9.74, 15.44	1.8, 27.4
λ (MoKα), Å	0.71073 (mon.)	0.71073 (mon.)
$\Delta\omega$, deg	$0.60 + 0.35 \tan\theta$	$0.85 + 0.35 \tan\theta$
Hor., ver. apert., mm	3.00, 4.00	3.21, 4.00
X-ray exposure, h	12.8	37.5
Reference reflections	$\bar{2}\ 2\ \bar{4}, \bar{1}\ 2\ \bar{4}, 1\ 2\ \bar{2}$	$2\ 3\ \bar{1}, 0\ \bar{2}\ \bar{3}, 4\ \bar{1}\ 1$
Data set	-12:12, 0:15, -13:13	-11:12,-10:14, -15:0
Total data	6153	5292
Total unique data	2904	5152
DIFABS corr. range		0.90, 1.16
Refinement		
No. of refined params	109	272
R[a]	0.0693 [for 1169 $F_o > 4.0\sigma F_o$]	0.0524 [for 3743 $F_o > 4.0\sigma F_o$]
$wR2$[a]	0.1004	0.1295
S	0.91	1.04
Weighting scheme[b]	$1/[\sigma^2(F^2) + (0.0455P)^2]$	$1/[\sigma^2(F^2) + (0.0594P)^2 + 0.64P]$
$(\Delta/\sigma)_{av}, (\Delta/\sigma)_{max}$	0.000, 0.001	0.000, 0.000
Min. and max. residual density, e Å^{-3}	$-0.43, 0.32$	$-0.46, 0.80$

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. – [b] $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

1.224 Å for aromatically substituted enones[17]. Second, the average value of the C–C bond length in aliphatically substituted enones is 1.468 Å[17]. Compound **3** shows an unexpectedly large C(1)–C(14) bond length of 1.523(6) Å which cannot be explained at the moment. The C(1)–C(8) bond of **4** [1.491(3) Å] is longer than the average value of 1.482 Å for aromatically substituted enones[17]. The P=C bond lengths of **3** and **4** do not deviate significantly from that of Mes*P=CCl_2 (**1**) [*d*(P=C): 1.666(3) Å][16]; while **4** [1.679(2) Å] has a slightly longer bond, that of **3** [1.658(4) Å] is even shorter than that of its non-conjugated model. If one would base the interpretation on these results only, **3** would appear to show no conjugation compared with conjugated β-carbon enones, and the indications of conjugation for **4** would be weak and uncertain. These phenomena will be discussed further below.

Calculations on Model β-Phosphaenones

In view of the unexpected outcome of the crystal structure analysis, it was desirable to investigate the structures by theoretical methods like high level ab initio calculations in order to obtain a deeper insight into this question. Acrolein has already been thoroughly studied in this respect[18–20] and Head-Gordon and Pople[21] have shown, that by using electron-correlation methods like MP2, relative energies of conformers and the rotation barriers are in

Table 4. Selected bond lengths (Å) and angles (°) of **3**, **4** and Mes*P=CCl_2 (**1**) (ESD in parentheses)

angles and bond lengths	**1**[a]	**3**	**4**
conformation	--	s-*cis*	s-*trans*
dihedral angle	--	0°	162.57(19)°
d(P=C)	1.666(3)	1.658(4)	1.679(2)
d(C(1)-C(8))	--	--	1.491(3)
d(C(1)-C(14)	--	1.523(6)	--
d(C=O)	--	1.207(6)	1.217(3)
C(1)-P-C(2)	102.63(15)	102.38(19)	103.57(11)
P-C(1)-Cl(1)	129.09(18)	124.3(2)	125.28(13)
Cl(1)-C(1)-Cl(2)	112.86(19)	--	--
Cl(1)-C(1)-C(8)	--	--	113.47(16)
Cl(1)-C(1)-C(14)	--	118.9(3)	–

[a] See ref.[16].

good agreement with experimental values. Wiberg et al.[8a] have found that atomic charges cannot be used as an indicator for conjugative effects, because the polarization of the π-electron density is compensated by σ-electron polarization in the opposite direction to minimize electron repulsion. This $\sigma-\pi$ interaction is also responsible for the small changes in bond lengths. Finally, Wiberg et al.[8b] have investigated several heterobutadienes and drew the conclusion that the barrier of rotation results mainly from the loss of π-electron delocalization, while the energy difference between *cis* and *trans* rotamer is caused by dipolar, lone pair–lone pair, and steric interactions.

To obtain information about conjugation in phosphaenones, we have performed ab initio calculations on all conformers and transition states of the parent phosphaacrolein (**12**) as well as of 3-phosphapropanal (**13**) and 3-hydroxy-1-phosphapropene (**14**) as reference structures.

Conformations and Barriers of Rotation

Geometry optimizations resulted in four planar phosphaacrolein structures as minima and two transition states, where the P=C–C and the C–C=O plane are located orthogonal to each other (Table 5). While the relative energy of the (*E*)-*exo* conformer [(*E*)-**12a**] is only 0.4 kcal/mol higher than that of the (*Z*)-*exo* structure [(*Z*)-**12a**] {at the HF level (*Z*)-**12a** is even more stable than [(*E*)-**12a**], the difference between the (*Z*)-*endo* [(*Z*)-**12b**] and (*E*)-*endo* [(*E*)-**12b**] stereoisomers is significantly larger (1.3 kcal/mol)}. This behavior reflects the repelling interaction between the oxygen (especially the oxygen lone pairs) and the substituent, and the lone pair at phosphorus, respectively. Wiberg et al. have found a similar effect for acrolein[8b]. Note that for **3**–**9** these differences will be dramatically influenced by the presence of the bulky Mes* group. For the transition structures, a difference of 0.9 kcal/mol has been found, which is unlikely to be caused by an interaction of the out-of-plane standing oxygen, but could be the result of the repulsion of a p_π orbital of the carbonyl carbon atom with the phosphorus lone pair. Of course, this effect is not as strong as in the *endo* structures and hence the energy difference lies between that of *endo* and *exo* rotamers. The obtained rotation barriers are very similar for (*E*) and (*Z*) isomers (maximum difference 0.5 kcal/mol), but are significantly different for the rotamers, i.e. 4.9 kcal/mol and 4.6 kcal/mol for *endo* and 6.5 kcal/mol and 7.0 kcal/mol for *exo* structures. Wiberg et al. have found similar values for acrolein (6.6 kcal/mol at the MP2/6-311++G**//MP2/6-31G* level of theory)[8b], which are in good accordance with experimental findings (6.5–7.0 kcal/mol)[22,23]. This indicates that the conjugation of phosphaacrolein and acrolein is of comparable magnitude.

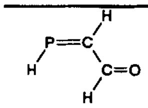
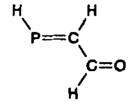
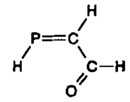
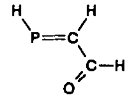
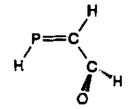
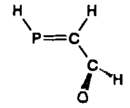
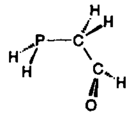
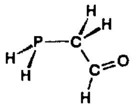
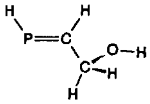
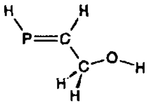
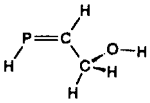
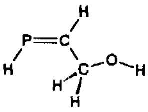
A comparison with the rotation barriers of our reference structures **13** and **14**, where conjugation is absent, should give evidence for the contribution of loss of π electron delocalization to the height of the barrier. The barrier for 3-phosphapropanal **13** (2.4 kcal/mol) is only about half that of phosphaacrolein **12**. For **13** the transition state shows a planar P–C–C=O skeleton, while in the equilibrium geometry, the P–C–C and the C–C=O plane are oriented perpendicularly. For the 3-hydroxy-1-phosphapropenes **14** barriers of 1.7 kcal/mol [(*E*) isomer] and 0.8 kcal/mol [(*Z*) isomer] have been found, and again the transition structures are planar, while the minima show eclipsed conformations. This behavior shows clearly, that in contrast to the reference systems, where the barriers are caused by steric effects, in phosphaacrolein **12** the barriers arise largely from the stabilization of the planar equilibrium geometry by conjugation of the two π-systems.

Bond Lengths, Bond Orders, and Orbital Interactions

As Wiberg et al.[8a] have already pointed out, differences in bond lengths of planar, conjugated and perpendicular, non-conjugated heterobutadienes are small. Indeed, the structural changes in phosphaacrolein and the reference structures are small but they are of recognizable magnitude to show the expected trends (see: Supplementary Material). The average P=C distance of $\bar{d}$(P=C) = 1.6889 Å for structures **12** is only 0.005 Å longer than $\bar{d}$(P=C) of the transition states **12**(TS) (1.6836 Å) and 0.008 Å longer than $\bar{d}$(P=C) of the reference structures **14** and **14**(TS) (1.6808 Å). The differences of $\bar{d}$(C=O) are even smaller, while deviations of $\bar{d}$(C–C) show the largest values (Table 6). The shortening of the double bonds and the elongation of the C–C single bonds in **12** occurs as one would expect for the loss of conjugation, but these effects are only small.

While the effects of conjugation on the structures are minimized by the already mentioned $\sigma-\pi$ interaction, the calculated bond orders (b.o.s.) and orbital interactions are not affected by this phenomenon. Hence, the changes of b.o.s. between the planar structures and the transition states are much more significant (Table 7). For the P=C bond, an average b.o. of 1.7891 has been found for **12** in contrast to 1.8686 in **12**(TS), where the π-systems are orthogonal and 1.8801 in **14** and **14**(TS), where a second π-system is missing. Similarly, the C=O double bond shows average b.o.s. of 1.7690 for **12** in contrast to 1.8308 for **12**(TS) and 1.8012 in **13**. It is obvious that in the planar systems the double bond character is significantly weaker than in the non-

Table 5. Structures, energies and rotation barriers of phosphaacrolein (**12**) and reference structures **13** and **14** obtained from ab initio calculations at the MP2(FULL)/6-31+G* and HF/6-31G* level (in parentheses)

Structure		Energy [a.u.]	ZPE [kcal/mol]	$E_{rel.}$ [kcal/mol]	$E_{rel.}$+ZPE [kcal/mol]	$E^{\ddagger}_{rot.}$ [kcal/mol]
	(*Z*)-**12a**	-493.586 028 2 (-493.014 730 6)	27.96544 (30.18021)	0.00000 (0.00000)	0.00000 (0.00000)	6.07811 (6.08723)
	(*E*)-**12a**	-493.585 343 0 (-493.014 341 0)	27.92433 (30.13989)	0.42997 (-0.24448)	0.39297 (-0.28077)	6.57205 (7.27771)
	(*Z*)-**12b**	-493.583 543 1 (-493.012 032 1)	27.89562 (30.16856)	1.56005 (1.60333)	1.49721 (1.59285)	4.58090 (4.49438)
	(*E*)-**12b**	-493.581 521 4 (-493.010 851 9)	27.81458 (30.09315)	2.82806 (2.43392)	2.69229 (2.35557)	4.27273 (4.64137)
	(*Z*)-**12**(TS)	-493.575 671 1 (-493.004 245 1)	27.49758 (29.63297)	6.49918 (6.57975)	6.07811 (6.08723)	-
	(*E*)-**12**(TS)	-493.574 198 6 (-493.002 743 6)	27.45525 (29.59685)	7.42319 (7.52196)	6.96502 (6.99694)	-
	**13**	-494.778 035 8 (-494.207 749 6)	41.48108 (43.93776)	0.00000 (0.00000)	0.00000 (0.00000)	2.38975 (2.02750)
	**13**(TS)	-494.773 886 8 (-494.203 952 0)	41.05529 (43.54273)	2.77296 (2.38303)	2.38975 (2.02750)	-
	(*E*)-**14**	-494.752 071 8 (-494.169 692 1)	43.04400 (45.92426)	16.46208 (23.88144)	17.86871 (25.66929)	1.71439 (1.16461)
	(*E*)-**14**(TS)	-494.748 876 1 (-494.167 449 7)	42.73184 (45.65479)	18.46742 (25.28857)	19.58310 (26.83390)	-
	(*Z*)-**14**	-494.751 723 6 (-494.169 810 5)	43.02093 (45.87064)	16.68058 (23.80715)	18.06645 (25.54674)	0.77500 (0.35080)
	(*Z*)-**14**(TS)	-494.749 993 3 (-494.168 878 0)	42.67562 (45.61834)	17.76636 (24.39230)	18.84145 (25.90482)	-

planar structures, which is caused by delocalization of π-electron density. The fact that the P=C bond is affected more by this conjugation shows that this bond is a better π-donor, which would also be expected from chemical intuition.

An even closer look into the bonding properties of molecules is possible by calculating the energy contributions of the interactions of single pairs of orbitals[24]. In our case the interactions of interest are those of the π- and π*-bond orbitals at the P=C and C=O bond, which could interact with π*-, σ*-, and lone-pair orbitals (Table 8).

While in the transition states (*E*/*Z*)-**14**(TS) and **13**(TS) definitely no interaction between P=C bond and C=O bond has been found, the π_{PC} to π^{*}_{CO} stabilization in the planar structures **12** is remarkably strong (30 kcal/mol). The back donation π_{CO} to π^{*}_{PC} gives an additional energy gain of about 7 kcal/mol and both interactions together prove that there is a significant stabilizing effect resulting from π-

Table 6. Average bond lengths and differences of average bond lengths (Å) (MP2/6-31+G*)

Structure	$\bar{d}$(P/C)	$\Delta\bar{d}$(P/C)	$\bar{d}$(C/O)	$\Delta\bar{d}$(C/O)	$\bar{d}$(C/C)	$\Delta\bar{d}$(C/C)
12	1.6889	-	1.2311	-	1.4749	-
12(TS)	1.6836	0.0053	1.2271	0.0040	1.4900	0.0151
14, **14**(TS)	1.6808	0.0081	-	-	-	-
13, **13**(TS)	-	-	1.2256	0.0055	-	-
13, **14**	-	-	-	-	1.4944	0.0195

Table 7. Vibrational frequencies and bond orders of phosphaacrolein and reference structures obtained from ab initio calculations at the MP2(FULL)/6-31+G* level

Structure	$\tilde{\nu}_{\text{min.}}$ [cm^{-1}]	$\tilde{\nu}$ (C=O) [cm^{-1}]	b.o. (P/C)	b.o. (C/C)	b.o. (C/O)
(*Z*)-**12a**	121	1704	1.8015	1.0870	1.7740
(*E*)-**12a**	134	1708	1.7956	1.0870	1.7667
(*Z*)-**12b**	87	1715	1.7845	1.0704	1.7691
(*E*)-**12b**	58	1716	1.7747	1.0790	1.7661
(*Z*)-**12**(TS)	-196	1723	1.8687	1.0157	1.8280
(*E*)-**12**(TS)	-188	1726	1.8684	1.0165	1.8335
13	89	1752	0.9044	1.0247	1.8012
13(TS)	-117	1751	0.9316	1.0017	1.8239
(*E*)-**14**	98	-	1.8738	1.0373	0.9066
(*E*)-**14**(TS)	-125	-	1.8828	1.0307	0.9148
(*Z*)-**14**	81	-	1.8784	1.0348	0.9084
(*Z*)-**14**(TS)	-99	-	1.8853	1.0293	0.9145

electron delocalization. In the transition states (*E*/*Z*)-**12**(TS) this conjugation breaks down, which is reflected by values between 0.7 and 2.2 kcal/mol for the π to π^* interactions. Here the π_{PC} to σ^*_{CO} delocalization becomes most important with values of about 6 kcal/mol. Because the reference structures (*E*/*Z*)-**14** show a similar π_{PC} to σ^*_{CO} stabilization, it is obvious that this delocalization is not comparable to an enone type of conjugation like in **12**.

Discussion

The results obtained from UV, IR, NMR spectroscopy, and calculations seem to tell us that there is conjugation between a P=C group and a C=O group in essentially the same way as in enones, where it is well-established. This conclusion is in line with that of Nyulászi et al. who state that the P=C moiety has a conjugative behavior similar to that of the C=C moiety[13]. In contrast, the X-ray crystal structures give no evidence for conjugation between the groups, as the bond lengths of the P=C, C−C, and C=O units are not significantly different from those in non-conjugated systems. This may be caused by σ−π interaction in which π-delocalization is compensated by a shift of σ-density in the opposite direction[8a]. In this context, it must be emphasized that certain β-C-enones also show C=O, C=C, and C−C bond lengths which do not differ much from the "nonconjugated values" [*d*(C=O) = 1.22 Å, *d*(C=C) = 1.34 Å, *d*(C−C) = 1.46 Å][17].

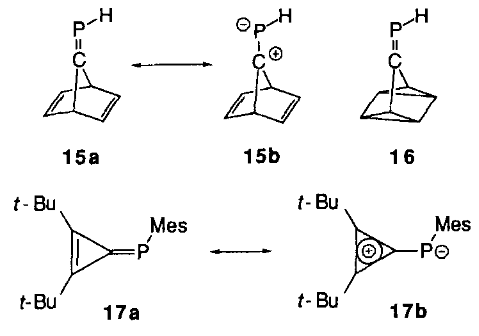
It is of interest to point out that these phenomena are not limited to phosphaenones, but are encountered in other compounds too, where the P=C unit is involved in different types of conjugation such as in 7-phosphanylidenenorbornadiene **15**[10] and phosphatriafulvene **17**[25] (Scheme 6).

Compound **15** [δ(^{13}P) = 89.9] and the corresponding quadricyclane **16** [δ(^{31}P) = 189.9] show a large difference in ^{31}P chemical shifts ($\Delta\delta$ = 100 ppm). This difference has been ascribed[10] to homoconjugative delocalization of electron density in the P=C bond, analogous to that in the 7-norbornadienyl cation[26] or, in closer analogy but to a lesser extent, in 7-methylenenorbornadienes[27]. In **15** the P=C π-bond may interact with the two C/C π-bonds of the bicyclic skeleton, which is impossible in **16** as it misses C=C bonds. As a consequence, a significant *d*(P=C) bond

Table 8. Natural bond orbital interactions MP2(FULL)/6-31+G* (kcal/mol)

Structure	$\pi_{PC} \rightarrow \pi_{CO}^*$	$\pi_{CO} \rightarrow \pi_{PC}^*$	$\sigma_{PC} \rightarrow \pi_{CO}^*$	$\sigma_{CO} \rightarrow \pi_{PC}^*$	$\pi_{PC} \rightarrow \sigma_{CO}^*$	$\pi_{CO} \rightarrow \sigma_{PC}^*$
(*Z*)-**12a**	28.89	8.08	-	-	-	-
(*E*)-**12a**	30.73	8.09	-	-	-	-
(*Z*)-**12b**	29.00	6.34	-	-	-	-
(*E*)-**12b**	29.95	6.17	-	-	-	-
(*Z*)-**12**(TS)	2.17	0.91	2.28	0.89	6.12	1.42
(*E*)-**12**(TS)	1.79	0.70	-	0.85	6.61	1.31
13	-	-	9.47	-	-	1.88
13(TS)	-	-	-	-	-	-
(*E*)-**14**	-	-	-	2.07	6.66	-
(*E*)-**14**(TS)	-	-	-	-	-	-
(*Z*)-**14**	-	-	-	1.97	5.68	-
(*Z*)-**14**(TS)	-	-	-	-	-	-

Scheme 6



lengthening and charge separation ($^{\delta-}$P–C$^{\delta+}$) would be expected in **15b**.

In order to test this qualitative reasoning, geometry optimizations of the model compounds **15** and **16** were performed at the HF/6-31G* level of theory. They resulted in structures (see: Supplementary Material), which are not in line with the above-mentioned expectations. The P=C bond of **15** (1.6651 Å) is shorter than that of **16** (1.6677 Å). While this difference is small, the bond orders show a much more significant weakening of the P=C bond in **16** (**15a**: 1.7727; **16**: 1.7435). This behavior may be an argument against remote delocalization, but a closer look at the structure shows that **16** is much more strained than **15**, which is reflected in a higher energy of 18 kcal/mol relative to **15**. The strained structure effects not only the energy but also the positions and directions of orbitals, which may result in better or worse overlap of bond forming orbitals. This might explain the elongation of the P=C bond in **16** and indicates, that from the bond lengths and b.o.s no information about a possible homoconjugation can be obtained. Similarly, the Mulliken population analysis of **15a** and **16** does not reveal significant homoconjugative electron displacement from the diene system to the P=C bond and certainly no increase of electron density on phosphorus. In **15a**, the normal P=C bond polarization is observed [P(0.053); C(−0.064)], while in **16**, the positive charge on carbon (0.048) does not differ much from that on phosphorus (0.058). It is evident that the observed large difference in ^{31}P chemical shifts cannot be caused by a simple contribution of charge density resulting from conjugative interactions as may in part be the case in the classical enones.

To elucidate the possible existence of a remote delocalization, an analysis of orbital interactions was performed. Indeed, two π_{CC} to π^*_{PC} interactions have been found to occur in **15a** with stabilizing energies of 5.83 kcal/mol each, but back donation does not occur and, as expected, no π to π* interaction has been found to exist in **16**. In contrast to phosphaacrolein **12**, where the P=C double bond acts as a donor, the π-system of the P=C bond in **15a** is the acceptor. Perhaps this reversal of direction of the remote delocalization is the key for understanding the unusual ^{31}P-NMR data of phosphaenones and phosphanorbornadiene, because π_{CC} to π^*_{PC} interaction could lead to a shielding, while a π_{PC} to π^*_{CO} interaction could produce a deshielding effect at the phosphorus atom. Again, more detailed theoretical investigations of the relation between electronic structure and NMR data are needed to clarify the observed effects.

Similarly conflicting evidence has been described by Regitz et al. for the phosphatriafulvene **17**[25] (Scheme 6). The ^{31}P chemical shift shows a dramatic shielding of the phosphorus nucleus [δ(^{31}P) = −23]. Mulliken population analysis of the parent unsubstituted phosphatriafulvene *does* show a charge shift towards phosphorus compared to a nonconjugated phosphaalkene. This is in line with a contribution of resonance structure **17b**, which is not surprising in view of the pronounced tendency of the three-membered ring to obtain the favorable status of an aromatic cyclopropenylium cation. In contrast, the P=C bond length of the tungstenpentacarbonyl complex of **17** has been found to be only 1.679 Å, a value which does not differ much from the average phosphaalkene bond length (1.67 Å); note that there is considerable evidence that the P=C bond length is not significantly influenced by this type of complexation[25]. Again, the origin of this discrepancy is not fully understood. Possibly, the Coulomb attraction between the separated charges contributes to counteract the bond lengthening caused by conjugation.

Empirically, we note that in three systems of rather divergent structural types, i.e. the β-phosphaenones **3** and **4**, the 7-phosphanylidenenorbornadiene **15**, and the phosphatriafulvene **17**, there is a strong effect on the ^{31}P chemical shift as expected for conjugation with the neighboring group: deshielding for **3** and **4**, strong shielding for **15** and **17**. For **17**, shielding qualitatively correlates with calculated changes of charge density, whereas for **3**, **4**, and **15**, it does not. Obviously, the contribution of other factors to the chemical shift tensor, in particular to the paramagnetic term, is decisive in many cases. This calls for a detailed analysis of the chemical shift tensors. Even more surprising is the lack of any significant effect on the relevant bond lengths in these systems. One must assume that this is a general trend in phosphaalkenes. In this regard, they behave in a similar fashion as other heterodienes[8a]. Perhaps the trend towards "conservation of structure" is even more pronounced for systems containing the P=C unit.

Conclusion

The synthesis of stable crystalline phosphaenones made the experimental investigation of these relatively unknown species possible. Comparison of β-P-enones with β-C-enones showed strong parallels in "enone behavior" as concluded from UV, NMR, and IR spectroscopy. Conjugation in phosphaenones results in deshielding of the phosphorus nucleus, together with a bathocromic shift of the n-π* transition in the UV spectrum, and a weakening of the C=O bond according to the IR spectrum. However, the P=C bond length is only slightly affected by conjugation as shown by the crystal data of **3** and **4**. Analogous "inertness" of the P=C bond length in reflecting delocalization of the π-electrons is observed in the 7-phosphanylidenenorbornadiene **15** and the phosphatriafulvene **17**. Therefore, the significance of bond lengths in (hetero)enones as an indicator of conjugation may be limited.

Calculations on model β-phosphaenones reveal a strong π_{PC} to π^*_{CO} stabilization of 30 kcal/mol. The π_{CO} to π^*_{PC} back donation gives an additional stabilization of 7 kcal/mol. This indicates there is an important electron delocalization which could be the physical source of the ^{31}P chemical shifts in conjugated phosphaenones.

The extent of conjugation in the enones is difficult to quantify. If we take the phosphorus chemical shift as a (questionable) measure of conjugation, the phosphaenones are only slightly conjugated, whereas the effect of conjugation on the phosphorus chemical shifts of **15** [δ(^{13}P) = 89] and of the phosphatriafulvene **17** [δ(^{31}P) = −23] is much larger.

Calculations on the nonsubstituted phosphaenone models **12** reveal some conjugation between the P=C and C=O π-systems, which is of comparable order to that of acrolein if the barrier of rotation is taken as criterion. It is evident that more work, both experimental and theoretical, is required to fully understand these interesting phenomena.

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Supplementary material of the calculations on **12**–**16** is available on request from the publisher on quoting the full journal citation.

Experimental

All experiments were performed in dried glassware and under nitrogen. Solvents were distilled from sodium benzophenone (THF) or lithium aluminium hydride (pentane). All solid starting materials were dried in vacuo. Liquids were distilled under N_2 prior to use. – NMR spectra were recorded with a Bruker AC 200 spectrometer (^{1}H, ^{13}C) or with a Bruker WM 250 spectrometer (^{31}P). Tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) was used as an external standard. – High-resolution mass spectra (HRMS) were recorded with a Finnigan MAT 5 spectrometer. The anhydride **7** and the silyl ester **8** were not subjected to elemental analysis due to their instability; HRMS confirmed the elemental composition. – UV spectra were recorded with a Beckman DU-64 spectrophotometer. – Infrared spectra were measured by using KBr pellets with a Matteson Galaxy 6030 FTIR. – Titrations were performed with a Mettler DL25 Titrator.

General Procedure for the Preparation of **3**–**5**: A solution of 2.5 ml of *n*-butyllithium in hexane (1.6 M; 4 mmol) was added dropwise to a suspension of 1.44 g (4 mmol) of dichloromethylene (2,4,6-tri-*tert*-butylphenyl)phosphane (**1**) in 25 ml of THF at −110 °C. The stirred mixture was warmed to −90 °C until a clear yellowish solution was obtained. To this solution 0.48 g (4 mmol) of pivaloyl chloride, 0.56 g (4 mmol) of benzoyl chloride, or 0.43 g (4 mmol) of ethyl chloroformate, were added at −90 °C. After warming of the reaction mixture to room temp. for 1 h, the solvent was evaporated. The residue was extracted with pentane and the extract filtered. Evaporation of the solvent from the filtrate followed by crystallization of the residue from pentane yielded pure **3**–**5**.

(Z)-[(Pivaloyl)chloromethylene](2,4,6-tri-tert-butylphenyl)-phosphane (**3**): Orange crystals, 1.35 g (83%), m.p. 127–129 °C. – ^{1}H NMR (C_6D_6): δ = 1.32 (s, 9H, *t*Bu), 1.37 [s, 9H, *p*-*t*Bu], 1.52 (s, 18H, *o*-*t*Bu), 7.59 [d, 2H, Ar, *J*(HP) = 1.7 Hz]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 28.2 [d, COC(CH_3)$_3$, *J*(CP) = 5.8 Hz], 31.4 [s, *p*-C(CH_3)$_3$], 32.9 [d, *o*-C(CH_3)$_3$, *J*(CP) = 6.8 Hz], 35.2 [s, *p*-*C*(CH_3)$_3$], 37.9 [s, *o*-*C*(CH_3)$_3$], 44.4 [s, CO*C*(CH_3)$_3$], 122.7 (s, *m*-Ar), 133.4 [d, *ipso*-Ar, *J*(CP) = 55.9 Hz], 151.6 (s, *p*-Ar), 154.0 [d, *o*-Ar, *J*(CP) = 2.7 Hz], 164.6 [d, P=*C*, *J*(CP) = 68.8 Hz], 201.8 [d, *C*=O, *J*(CP) = 19.9 Hz]. – ^{31}P NMR (C_6D_6): δ = 292. – IR (KBr): $\tilde{\nu}$ = 1643 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 208 nm (4.507), 240 (4.084), 300 (3.849). – MS (70 eV); *m/z* (%): 409 (3) [(M + H)$^+$], 408 (1) [M$^+$], 373 (12) [M$^+$ – Cl], 351 (71) [M$^+$ – *t*Bu]. – HRMS: calcd. for $C_{24}H_{38}PO^{35}Cl$ 408.2349, found 408.2352. – $C_{24}H_{38}POCl$ (409.0): calcd. C 70.48, H 9.37, O 3.91; found C 70.56, H 9.46, O 3.78.

(Z)-[(Benzoyl)chloromethylene](2,4,6-tri-tert-butylphenyl)-phosphane (**4**): Yellow crystals, 1.51 g (88%), m.p. 109–111 °C. – ^{1}H NMR (C_6D_6): δ = 1.32 (s, 9H, *p*-*t*Bu), 1.47 (s, 18H, *o*-*t*Bu), 7.14–7.18 (m, 3H, Ph), 7.59 [d, 2H, Ar, *J*(HP) = 1.5 Hz], 7.87–7.91 (m, 2H, Ph). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 31.4 [s, *p*-C(CH_3)$_3$], 32.9 [d, *o*-C(CH_3)$_3$, *J*(CP) = 6.8 Hz], 35.2 [s, *p*-*C*(CH_3)$_3$], 37.9 [s, *o*-*C*(CH_3)$_3$], 122.8 (s, *m*-Ar), 128.3 (s, *m*-Ph), 129.9 [d, *o*-Ph, *J*(CP) = 5.2 Hz], 132.2 (s, *p*-Ph), 133.6 [d, *ipso*-Ar, *J*(CP) = 56.1 Hz], 138.8 (s, *ipso*-Ph), 151.9 (s, *p*-Ar), 153.7 [d, *o*-Ar, *J*(CP) = 2.7 Hz], 167.1 [d, P=*C*, *J*(CP) = 71.4 Hz], 190.0 [d, *C*=O, *J*(CP) = 30.4 Hz]. – ^{31}P NMR (C_6D_6): δ = 321. – IR (KBr): $\tilde{\nu}$ = 1649 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 207 nm (4.593), 305 (4.042). – MS (70 eV); *m/z* (%): 428 (2) [M$^+$], 393 (2) [M$^+$ – Cl], 371 (65) [M$^+$ – *t*Bu]. – HRMS: calcd. for $C_{26}H_{34}PO^{35}Cl$ 428.2036, found 428.2038. – $C_{26}H_{34}POCl$ (429.0): calcd. C 72.79, H 7.99, O 3.73; found C 72.70, H 8.04, O 3.61.

Ethyl (Z)-2-Chloro-2-(2,4,6-tri-tert-butylphenylphosphanylidene)-acetate (**5**): Yellowish crystals, 1.36 g (86%), m.p. 98–101 °C. – ^{1}H NMR (C_6D_6): δ = 0.98 [t, 3H, C*H*$_3$, *J*(HH) = 7.10], 1.31 (s, 9H, *p*-*t*Bu), 1.50 (s, 18H, *o*-*t*Bu), 4.50 [q, 2H, C*H*$_2$, *J*(HH) = 7.11], 7.59 [d, 2H, Ar, *J*(HP) = 1.6 Hz]. – ^{13}C{^{1}H} NMR (C_6D_6): δ = 14.1 (s, CH_3), 31.4 [s, *p*-C(CH_3)$_3$], 32.9 [d, *o*-C(CH_3)$_3$, *J*(CP) = 7.3 Hz], 35.1 [s, *p*-*C*(CH_3)$_3$], 38.0 [s, *o*-*C*(CH_3)$_3$], 62.2 (s, CH_2), 122.8 (s, *m*-Ar), 133.9 [d, *ipso*-Ar, *J*(CP) = 53.6 Hz], 151.7 (s, *p*-Ar), 153.8 [d, *o*-Ar, *J*(CP) = 2.8 Hz], 156.9 [d, P=*C*, *J*(CP) = 67.0 Hz], 164.2 [d, *C*=O, *J*(CP) = 24.6 Hz]. – ^{31}P NMR (C_6D_6): δ = 312. – IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 209 nm (4.504), 237 (4.070), 293 (3.988). – MS (70 eV); *m/z* (%): 396 (1) [M$^+$], 381 (1) [M$^+$ – CH_3]. – HRMS: calcd. for $C_{22}H_{34}PO_2{}^{35}Cl$ 396.1985, found 196.1986. – $C_{22}H_{34}POCl$ (396.9): calcd. C 66.57, H 8.64, O 8.06; found C 66.57, H 8.69, O 7.77.

Lithium (Z)-2-Chloro-2-(2,4,6-tri-tert-butylphenylphosphanylidene)acetate (**6**): 1.44 g (4 mmol) of compound **1** was dissolved in 25 ml of THF and lithiated (see general procedure). At −110 °C, excess CO_2 gas from dry ice was sublimed into the reaction mixture. The mixture was warmed to room temp. for 1 h to give a yellowish solution of **6**. This solution was used for the synthesis of **7**–**9**. Compound **6** could be isolated by evaporation of the solvent. The residue was washed with pentane furnishing **6** as a slightly yellowish powder. Yield: 1.43 g, (96%). – ^{1}H NMR ([D$_8$]THF): δ = 1.22 (s, 9H, *p*-*t*Bu), 1.37 (s, 18H, *o*-*t*Bu), 7.31 (s, 2H, Ar). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 31.6 [s, *p*-C(CH_3)$_3$], 32.9 [d, *o*-C(CH_3)$_3$, *J*(CP) = 7.2 Hz], 35.5 [s, *p*-*C*(CH_3)$_3$], 38.4 [s, *o*-*C*(CH_3)$_3$], 122.6 (s, *m*-Ar), 138.3 [d, *ipso*-Ar, *J*(CP) = 55.7 Hz], 150.4 (s, *p*-Ar), 153.5 (s, *o*-Ar), 168.2 [d, *C*=O, *J*(CP) = 21.7 Hz], 171.1 [d, P=*C*, *J*(CP) = 62.1 Hz]. – ^{31}P NMR ([D$_8$]THF): δ = 282. – IR (KBr): $\tilde{\nu}$ = 1614 cm^{-1}, 1363 cm^{-1}. – UV (ethanol): λ_{max} (lg ε) = 207 nm (4.472), 241 (4.162), 290 (3.912).

General Procedure for the Synthesis of **7** *and* **8**: To a crude solution of the carboxylate **6** 0.48 g (4 mmol) of pivaloyl chloride or 0.43 g (4 mmol) of trimethylsilyl chloride, respectively, was added at room temp. The mixture was stirred for 30 min at ambient temp. The solvent was evaporated in vacuo. The residue was extracted with pentane and the extract filtered. Evaporation of the solvent from the filtrate followed by crystallization of the residue from pentane yielded pure **7** or **8**.

(Z)-2-Chloro-2-(2,4,6-tri-tert-butylphenylphosphanylidene)acetyl 2,2-Dimethylpropionate (**7**): Yellowish crystals, 1.37 g (76%), m.p. 105–108 °C. – ^{1}H NMR (C_6D_6): δ = 1.19 (s, 9H, *t*Bu), 1.28 (s, 9H, *p-t*Bu), 1.42 (s, 18H, *o-t*Bu), 7.54 [d, 2H, Ar, *J*(HP = 1.6 Hz]. – $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 26.6 (s, *t*Bu*C*H_3), 31.3 [s, *p*-C(*C*H_3)$_3$], 33.0 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 7.2 Hz], 35.2 [s, *p*-*C*(CH_3)$_3$], 37.9 [s, *o*-*C*(CH_3)$_3$, 39.8 (s, *t*Bu)], 123.0 (s, *m*-Ar), 132.5 [d, *ipso*-Ar, *J*(CP) = 52.9 Hz], 152.4 (s, *p*-Ar), 153.8 [d, *o*-Ar, *J*(CP) = 2.8 Hz], 155.5 [d, P=*C*, *J*(CP) = 69.1 Hz], 160.5 [d, *C*=O, *J*(CP) = 28.6 Hz], 173.9 (s, *C*=O). – ^{31}P NMR (C_6D_6): δ = 341. – IR (KBr): $\tilde{\nu}$ = 1784 cm^{-1} (C=O), 1728 cm^{-1} (C=O). – MS (70 eV); *m/z* (%): 452 (1) [M^+], 396 (6) [M^+ – *t*Bu], 351 (13) [M^+ – *t*Bu – CO_2]. – HRMS: calcd. for $C_{25}H_{38}PO_3{}^{35}Cl$ 452.2247, found 452.2251.

Trimethylsilyl (Z)-2-Chloro-2-(2,4,6-tri-tert-butylphenylphoshanylidene)acetate (**8**): Yellowish powder, 1.45 g (82%), m.p. 163–165 °C. – ^{1}H NMR (C_6D_6): δ = 0.33 [s, 9H, Si(CH_3)$_3$], 1.32 (s, 9H, *p-t*Bu), 1.50 (s, 18H, *o-t*Bu), 7.59 [d, 2H, Ar, *J*(HP) = 1.5 Hz]. – $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = –0.2 [s, Si(CH_3)$_3$], 31.3 [s, *p*-C(*C*H_3)$_3$], 32.9 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 7.1 Hz], 35.1 [s, *p*-*C*(CH_3)$_3$], 37.9 [s, *o*-*C*(CH_3)$_3$], 122.8 (s, *m*-Ar), 134.4 [d, *ipso*-Ar, *J*(CP) = 53.9 Hz], 151.6 (s, *p*-Ar), 153.6 [d, *o*-Ar, *J*(CP) = 2.6 Hz], 158.7 [d, P=*C*, *J*(CP) = 67.9 Hz], 163.6 [d, *C*=O, *J*(CP) = 26.2 Hz]. – ^{31}P NMR (C_6D_6): δ = 318 ppm. – IR (KBr): $\tilde{\nu}$ = 1695 cm^{-1} (C=O). – MS (70 eV); *m/z* (%): 440 (2) [M^+], 425 (5) [M^+ – CH_3], 383 (12) [M^+ – *t*Bu]. – HRMS: calcd. for $C_{23}H_{38}PO{}^{28}Si{}^{35}Cl$ 440.2067, found 440.2066.

(Z)-2-Chloro-2-(2,4,6-tri-tert-butylphenylphosphanylidene)acetic Acid (**9**): – *From carboxylate* **6**: To compound **6** (4 mmol) 25 ml of water and 25 ml of chloroform were added. The "milky" emulsion was acidified with hydrochloric acid (1 M) until the aqueous layer reached pH = 1. The yellow chloroform layer was separated and the solvent evaporated to furnish **9**. The carboxylic acid was purified by crystallization from acetonitrile affording slightly yellowish crystals. Yield 1.24 g (85%).

From silyl ester **8**: 0.96 g (2.16 mmol) of compound **8** was dissolved in 20 ml of chloroform; then 0.5 ml of water was added. The reaction mixture was vigorously stirred at ambient temp. for 15 min. Concentration in vacuo yielded a slightly yellow solid. The solid was washed with pentane and dried in vacuo yielding 0.80 g (100%) of **9**. M.p. 173–175 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 9H, *p-t*Bu), 1.40 (s, 18H, *o-t*Bu), 7.40 (s, 2H, Ar), 10.90 (s, 1H, OH). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 31.1 [s, *p*-C(*C*H_3)$_3$], 32.7 [d, *o*-C(*C*H_3)$_3$, *J*(CP) = 7.1 Hz], 34.9 [s, *p*-*C*(CH_3)$_3$], 37.8 [s, *o*-*C*(CH_3)$_3$], 122.5 (s, *m*-Ar), 132.6 [d, *ipso*-Ar, *J*(CP) = 53.3 Hz], 151.6 (s, *p*-Ar), 153.0 (s, *o*-Ar), 153.1 [d, P=*C*, *J*(CP) = 68.9 Hz], 169.5 [d, *C*=O, *J*(CP) = 27.4 Hz]. – ^{31}P NMR ($CDCl_3$): δ = 332. – IR (KBr): $\tilde{\nu}$ = 1691 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 209 nm (4.307), 242 (4.041), 290 (3.822). – MS (70 eV); *m/z* (%): 369 (7) [$(M + H)^+$], 351 (3) [$(M + H - H_2O)^+$]. – HRMS: cacld. for $C_{20}H_{30}PO_2{}^{35}Cl$ 368.1672, found 368.1673. – $C_{20}H_{30}PO_2Cl$ (368.9): calcd. C 65.12, H 8.20, O 8.67; found C 64.62, H 8.21, O 8.56.

X-ray Structure Analysis of **3** *and* **4**: Yellow crystals of **3** (monoclinic) and **4** (triclinic) were obtained by recrystallization from pentane (mixed isomers). The single-crystal X-ray structures of compounds **3** and **4** were determined. ORTEP plots are given in Figures 1 and 2, respectively. Crystallographic data are shown in Table 3, bond lengths and angles for selected non-hydrogen atoms of **3** and **4** are compiled in Table 4. Yellow crystals of compound **3** and **4** were first cut and then mounted on a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4 T diffractometer on a rotating anode. Compound **4** was cooled in a cold nitrogen stream. Data were corrected for *Lp* effects and for a linear decay of 13% and 15% of the reference reflections for **3** and **4**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry[28]. For **4** an empirical absorption correction (DIFABS[29]) was applied as implemented in PLATON[30]. F_c values of **3** were corrected for secondary extinction by refinement of an empirical isotropic parameter: $F'_C = F_c[1 + xF_c^2\lambda^3/\sin(2\Theta)]^{-1/4}$, with $x = 13(3) \cdot 10^{-6}$. Both structures were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF–92[31]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[32]); no observation criterion was applied during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms, by a factor of 1.5 for the methyl and 1.2 for the aromatic hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. The highest remaining electron density found in compound **4** was near the disordered *tert*-butyl group. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography[33]. For further details see ref.[34]

Computational Methods: All structures have been fully optimized at HF/6-31G* and MP2-Fu/6-31+G* level of theory by using the program package GAUSSIAN 92[35]. Stationary points were characterized as real minima and real transition states by performing frequency calculations resulting in zero or one imaginary frequency, respectively. Energies were calculated relative to the lowest rotamer and corrected for zero-point vibrational energies, which were scaled by the factor of 0.90 for better agreement with experimental data[36]. With the MP2-optimized structures NBO analyses[37] were carried out by using the SCF density to calculate natural charges, natural bond orbitals (NBOs) and bond orders. The bond orders were obtained as the sums of squares of off-diagonal density matrix elements between pairs of atoms in the NBO basis, which follows the method of Wiberg bond index[38]. Orbital interactions were calculated by second-order perturbation theory of the NBO Fock matrix resulting in energies for the stabilizing donor-acceptor interactions of "filled" Lewis-type NBOs and "empty" non-Lewis-type NBOs.

Titrations: The pk_a of benzoic acid, acrylic acid and **9** were determined by titrating a solution of the acid in 85.6 (wt-% ethanol/water with 0.1002 M NaOH (aq). The pk_a was determined at the half equivalence point where pH = pk_a.

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