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SYNTHESIS AND STRUCTURE OF ARYL-SUBSTITUTED PHOSPHA-ALKENES

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Abstract—An improved synthesis of the two triarylsubstituted phospha-alkenes mesityl (diphenylmethylene)phosphine (**1a**) and 2,6-dimethylphenyl(diphenylmethylene)phosphine (**1b**) is described. Of several variants, the preferred route starts with the aryl bromides **4** which are converted to the corresponding Grignard reagents and to the arylphosphonous diamides **7** which with PCl_3 yield arylphosphonous amide chlorides **9** thence phosphinous amides **10** and to the phosphinous chlorides **11** which with DBU eliminate HCl to furnish the title compounds in 60–85% yield. The chemical and spectral data of **1a** and **1b** are discussed; they contain essentially localized P=C bonds and are stabilized mainly by steric protection. These conclusions are confirmed by HFS-calculations on simple model compounds (**17**, **16'**, **18**, **19** and **20**) which identify the phosphorus lone pair as HOMO and the π-orbital as NHOMO; however, both orbitals are close in energy. Furthermore, the calculations reveal the importance of phosphorus d-orbitals in bonding, and the polarization in the P=C bond (P as positive pole) which had earlier been derived from chemical evidence. Finally, it is shown that interaction of the P=C bond with phenyl groups does not dramatically influence the bonding situation, but substitution by a heteroatom (nitrogen substituted on carbon; **20**) does.

Of particular interest in the crystal and molecular structure of **1a** are the short P=C bond length (1.692(3)Å) and the Mes-P-C bond angle (107.5°); the latter is smaller than expected (and found) for purely sp^2-hybridized atoms, but larger than the unsubstituted parent compound $HP{=}CH_2$ (**16**).[3] It is also noteworthy that the structure of **1a** is essentially unchanged on complexation to metal centres.

The empirical "double bond rule"[1] states that second and higher row elements do not form stable compounds in which they are involved in double bonding of the $p\pi$–$p\pi$ type. For trivalent phosphorus this implies that phospha-alkenes (or methylenephosphines), in which phosphorus has the coordination number 2, are expected to be unstable, and indeed, until about 20 years ago, they were practically unknown.

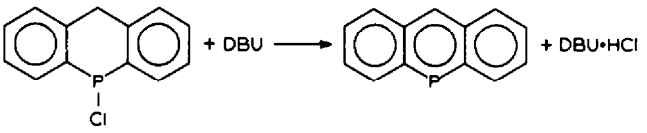
In the meantime, an ever-increasing number of compounds containing $3p\pi$-hybridized phosphorus have been prepared,[2] and their study has allowed two important conclusions. In the first place, the double bond rule is essentially correct in so far as simple "unprotected" phospha-alkenes such as $PH{=}CH_2$,[3] or phospha-alkynes such as $P{\equiv}CH$,[4] proved to be unstable at room temperature. Equally important is the second conclusion that the $p\pi$-hybridized state of phosphorus can be stabilized by one (or a combination) of the following approaches: (a) incorporation into a delocalized system,[5–11]. (b) incorporation into a charged system,[9–11] (c) complexation to a metal centre,[12] (d) steric protection by bulky substituents.

The first three approaches achieve stabilization mainly by increasing the thermodynamic stability of the compounds, be it by different mechanisms. The last approach, which prevents the normally observed dimerization or polymerization of simple phospha-alkenes by steric hindrance, is of kinetic nature. It is particularly attractive if one is interested in a picture of the P=C unit that is essentially unblurred by resonance effects. It was with this goal in mind that in 1978 we prepared mesityl (diphenylmethylene)-phosphine (**1a**), the first stable phospha-alkene bearing only carbon substituents and owing its stability primarily to steric protection and not to electronic factors.[13] In this paper, we wish to report details and progress on the synthesis of **1a** and of its lower homologue 2,6-dimethylphenyl (diphenylmethylene)phosphine (**1b**), and to discuss their structure and properties against the background of theoretical calculations and the crystal structure of **1a**. In contrast to **1a** and **1b**, the less substituted lower homologues 2-methylphenyl(diphenylmethylene) phosphine (**1c**) and phenyl(diphenylmethylene) phosphine (**1d**) could not be isolated due to polymerization.[8b,13]

RESULTS AND DISCUSSION

Synthesis of tris-arylsubstituted phospha-alkenes

In our studies[2b] on the synthesis of phospha- and arsa-aromatic analogues of naphthalene, anthracene and phenanthrene, the elimination of HCl from a chlorodihydroaromatic precursor by tertiary amines had proven to be a valuable and general approach to these aromatic derivatives of two-coordinate phos-

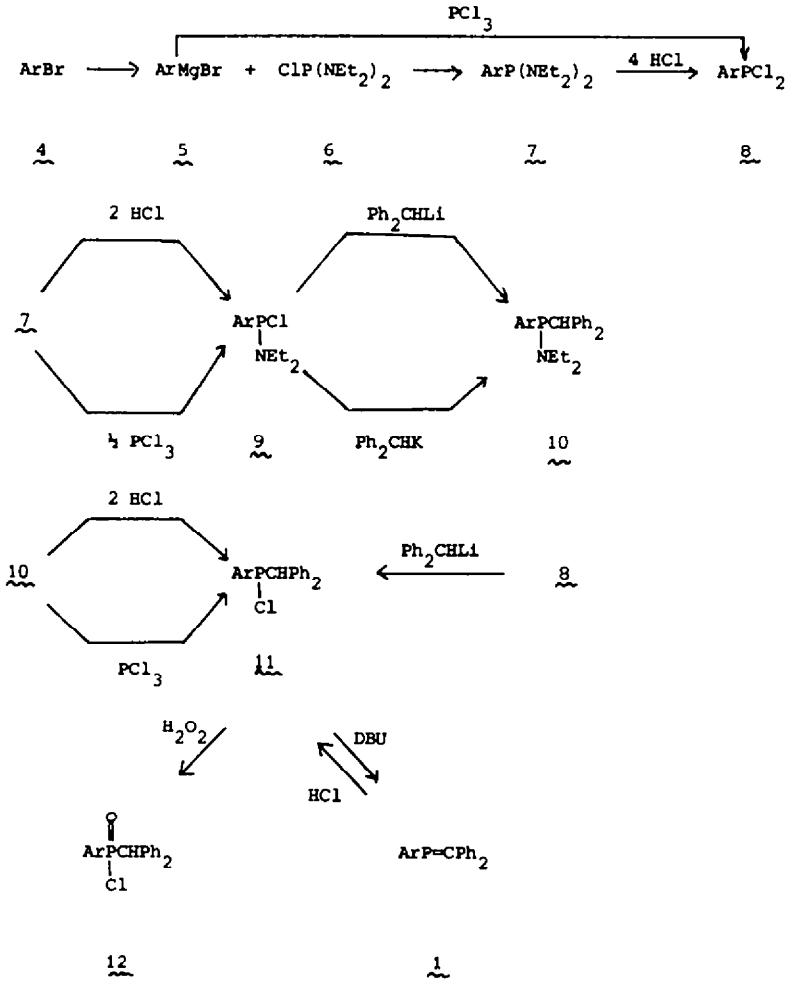


2 3

phorus, as illustrated by the conversion of **2** to **3**.[14]

Encouraged by the results in the aromatic series, we envisaged an analogous approach for the preparation of the then unknown stable phospha-alkenes by elimination of HCl from a chlorophosphine such as **11**. Scheme 1 presents a survey of the routes followed for the preparation of these precursors **11** and of **1**.

Starting point are the aryl bromides **4**. Originally, we obtained **11** by coupling the corresponding Grignard reagents **5** with PCl_3 to **8** which on reaction with diphenylmethyllithium gave **11**. Although this route appears to be convenient by its shortness, the yields in both steps were not reliable and the removal of impurities was difficult. The principal side product encountered in the coupling of **5** and PCl_3 was Ar_2PCl, while in the second step diphenylmethane was a tenacious impurity. For these reasons we now usually prefer the more roundabout, but controllable, approach (Scheme 1). First, **5** is coupled with chlorobis(diethylamino)phosphine (**6**) to yield the arylphosphonous diamides **7**; **7** may be converted to **8** by treatment with 4 equivalents of HCl in ethereal



a: Ar = 2,4,6-trimethylphenyl (= mesityl = Mes)
b: Ar = 2,6-dimethylphenyl (= xylyl)
c: Ar = 2-methylphenyl
d: Ar = phenyl

Scheme 1.

solvents. However, it was advantageous to replace only one amino substituent in **7** with exactly 2 equivalents of HCl in THF or, more conveniently, with 0.5 equivalents of PCl_3. This reaction afforded **9**, in which the chlorine could be selectively substituted by the diphenylmethyl anion to furnish **10**. Although the lithium derivative, easily obtained from diphenylmethane and n-butyllithium in THF, can be applied for this reaction, the potassium derivative was superior in our hands. It is obtained quantitatively and with comparable ease by Ziegler-cleavage of diphenylmethyl ethyl ether,[15] gives no diphenylmethane as side product and is definitely superior for substituted diphenylmethyl derivatives.[16] By careful addition of 2 equivalents of HCl in diethyl ether/THF to **10**, **11** can be prepared; however, HCl tends to cleave the diphenylmethyl group from phosphorus. Use of PCl_3 gave a purer product **11**. As **11** partially decomposed on distillation, crystallization from pentane was the method of choice for its purification.

In small runs, elimination of HCl from **11** was performed in an evacuated and sealed system; larger runs were performed under nitrogen: In THF solution with a slight excess of DBU, the reaction proceeded nearly quantitatively (NMR) at room temperature after 1–3 h. Purification of **1** can be achieved by filtration from DBU · HCl and evaporation of the filtrate; we then preferentially apply column chromatography on silica gel with diethyl ether as eluent followed by crystallization from pentane (see **1b** in the Experimental). Alternative ways of work-up include extraction of the residue with cyclohexane or pentane, followed by distillation and crystallization (cyclohexane or pentane). By these procedures, **1a** and **1b** were obtained on a 50 g scale in 60–85% yield, based on **11**; the melting points are 81–85°[17] and 75.5–80°, respectively.

Attempts to synthesize the lower homologues **1c** and **1d** analogous treatment of **11c** and **11d** with DBU resulted in the rapid formation of a white precipitate of DBU · HCl which indicates that the expected elimination of HCl had readily occurred. However, the desired products **1c** and **1d** were apparently too unstable to be isolated under our conditions; instead, ^1H NMR spectra with broad signals around 7 ppm (**1c** and **1d**) and 1.5 ppm (**1c**) indicated the formation of polymeric products. In the meantime, Becker, Uhl and Wessely have obtained **1d** by a different route; it was characterized by its NMR spectra, but was too unstable to be isolated.[8b]

Properties of **1a** *and* **1b**

The phosphaethenes **1a** and **1b** were thermally stable compounds; **1a** was distillable at 140°/10^{-3} mbar. At room temperature, they are relatively inert against water or against dry oxygen,[18] but in $CDCl_3$ solution moist air slowly leads to decomposition; under these conditions, **1a** furnished $MesPH(=O)CHPh_2$ (**13**) as the only identified product; presumably, the formation of **13** occurs by addition of water to the P=C bond[19] under the influence of HCl (from H_2O and $CDCl_3$).

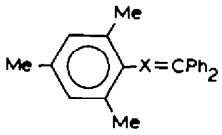
The chemical reactivity of **1a** and **1b** will not be discussed in detail here, as it will be[16] or has been[12c,d,13,18–21] the subject of several publications. Suffice it to say that at the level of our present understanding, the P=C bond is polarized so that phosphorus is the positive pole, as one would expect from electronegativity considerations. This was concluded from the reaction of **1** with polar reagents,[13,18–21] exemplified by the reaction of **1a** with HCl to furnish **11a** (Scheme 1); this reaction must be carried out at −60° in order to avoid further cleavage of **11a** by HCl to **8a** and diphenylmethane. A similar orientation had already been observed by Gier for the addition of HCl to P≡CH.[4] It should be emphasized that this polarization of the P=C bond is opposite to that of the N=C bond.[22] Other reactions, e.g. with O_2, S_8, H_2O_2,[18] Se,[21] $THF \cdot Cr(CO)_5$,[12c] $Pt(PPh_3)_2(C_2H_4)$,[12d] and CH_3I[20] are initiated by attack at phosphorus. These latter reactions can be understood by assuming a frontier orbital controlled mechanism, as theoretical calculations show the HOMO in phospha-alkenes to be the lone pair at phosphorus (*vide infra*). Finally, it should be pointed out that the regiochemistry of **1** has so far been discussed in terms of electronic factors only; in view of the steric congestion around the phosphorus atom, certain reactions may also be controlled by steric effects. This probably holds to a lesser degree for the reactions mentioned above, but it may become important, e.g. in cycloaddition reactions.[16] With such a delicate interplay of different effects, the prediction of the regiochemistry of phospha-alkenes, though feasible to a certain extent, remains difficult.

Like the chemical reactivity, the spectral data were very informative concerning the structure of **1**. Most characteristic are the NMR spectra. The low field chemical shift of both phosphorus (**1a**: δ = 233.0 ppm; **1b**: δ = 232.5 ppm) and carbon (**1a**: δ = 193.4 ppm, **1b**: δ = 193.6 ppm) established the presence of the P=C unit. The identity of the carbon atom was corroborated by the strong enhancement of its signal in the ^{13}C NMR spectrum of $MesP=^{13}CPh_2$ (**1a**-$^{13}\dot{C}$) which was synthesized as **1a** using diphenylmethane-α-$^{13}\dot{C}$ for the conversion of **9** to **10**-$^{13}\dot{C}$ (Scheme 1 and Experimental). The chemical shift of this carbon atom is surprisingly low and comparable to those of carbonyl carbon atom; similarly low chemical shifts are observed for other phospha-alkenes.[2d] As far as we are aware, the reason for this very low field shift of carbon is not well understood.[2e] It can certainly not be explained by charge effects, as intuition and calculation (*vide infra*) predict more negative charge on carbon for a P=C bond compared to a C=C bond.

In our preliminary communication,[13] we erroneously assumed evidence for hindered rotation around the aryl-phosphorus bond in **1** from the double occurrence of *ortho*-methyl carbon signals; it was particularly misleading that in both **1a** and **1b**, the second set of signals (a doublet at δ = 22.7 ppm in the spectrum of **1a**; a doublet at δ = 22.8 ppm in the spectrum of **1b**) were accidentally of the same height as the proper signals (**1a**: 22.1 ppm; **1b**: 22.2 ppm). On further purification,[17] it turned out that the former signals do not belong to **1a** or **1b**. The identity of the impurities is still mysterious, as all their other signals (^1H, ^{13}C, ^{31}P) apparently coincide with those of **1a** or **1b**. Thus, we must conclude that the NMR spectra do not furnish direct information on steric hinderance in **1**; however, this matter will be addressed later on.

Table 1. Absorption maxima of **1a**, **1b**, **14** and **15** in THF

	1a	1b	14	15
λ_{max}				267 (3.06)
[nm]	254 sh (3.20)	282 sh (2.42)	275 sh (3.29)	273 sh (3.02)
(log ε)	324 (2.84)	322 (2.60)	360 (2.92)	290 sh (2.70)



14 : X = N
15 : X = CH

The UV spectra of **1a** and **1b** are compared with those of the nitrogen- and carbon-analogue of **1a**, **14**[23] and **15**, respectively, in Table 1. The UV-spectra of the phospha- and aza-alkenes (imines) are quite similar. The bands at 324, 322 and 360 nm, respectively, are probably due to $n \rightarrow \pi^*$ transitions; this assignment is supported by the theoretical calculations and by the absence of this band in the spectrum of **15** and of the Cr(CO)-complex of **1a**.[12c]

The IR spectra of **1a**, **1b**, **14** and **15** are very similar, except for one absorption in the 900 cm^{-1} region of **1a** and **1b** which we tentatively assigned to the stretching vibration of the P=C bond. This assignment is based on the HFS calculations which for $HP{=}CH_2$ (**16**[1]) predict $\nu(P{=}C) = 940\ cm^{-1}$; relative to $\nu(N{=}C)$ (for **14**: $\nu \approx 1615\ cm^{-1}$), such a bathochromic shift is in the expected range. The value also compares reasonably well with that of 896 cm^{-1} assigned to the P=N bond of an aminoiminophosphine.[7a] A band at 1200 cm^{-1} has been assigned to an oxygen-substituted P=C bond.[8a] An additional argument in favour of this assignment is the shift of the band from $\bar{\nu} = 917\ cm^{-1}$ in **1a** to $\bar{\nu} = 907\ cm^{-1}$ in **1a**-^{13}C (see Experimental).

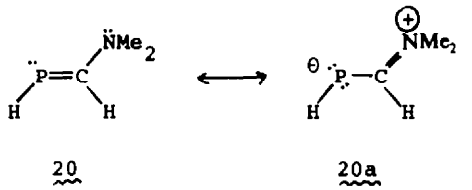
As pointed out, **1a** and **1b** are thermally stable compounds. In contrast, **1c** and **1d** could not be isolated, presumably because they polymerized[8b] after formation. This difference in stability between phospha-alkenes carrying two *ortho*-methyl groups and those which carry one or none can serve as a strong argument that it is mainly steric protection which (kinetically) stabilize the P=C bond in **1a** and **1b**. Models, and the crystal structure of **1a** (*vide infra*), suggest that the 2,6-disubstituted aromatic rings on phosphorus are forced into a position which is nearly perpendicular to that of the P=C nodal plane. In this conformation, conjugative interaction between ring and P=C bond is minimal; only inductive and steric factors can be operative. The inductive effects are expected to be essentially the same for **1a–d**. This is also the case for the influence of the two phenyl groups on carbon; although they may adopt intermediate conformations and thus develop a certain degree of conjugative interaction, this interaction will be approximately equal in **1a–d**, or probably even stronger in **1c** and **1d** where they can better approach coplanarity. Similarly, models show that in **1c** and **1d** there is practically no steric inhibition for coplanarity between the P-aryl ring and the P=C nodal plane; therefore, if conjugative interaction of the aromatic rings with the P=C system were decisive for stability, **1c** and **1d** would be expected to be more stable than **1a** and **1b**. The order of stability actually found is the reverse one. This proves the predominant role of steric protection; conjugation is not fully absent (see theoretical section), but it is neither sufficient nor essential for thermal stability in the all-carbon-substituted phospha-alkenes. The situation is completely different for heterosubstituted phospha-alkenes; according to both experimental[8] and theoretical evidence, conjugation here plays a major role in determining the stability of the compounds.

It should, however, be emphasized that the kinetic instability of compounds such as **1c**, **1d** or $HP{=}CH_2$ (**16**)[3] does not imply inherent thermodynamic instability; all it means is that they do not survive under conditions where oligomers, polymers or other reaction products can be formed, the single bonds of which are more stable than the P=C bond from which they are derived. On the contrary, a certain qualitative indication for the thermodynamic stability of **1a** and **1b** may be derived from the 70 eV electron impact mass spectra in which the molecular ions have high relative intensities ($\mathbf{1a}^+$ 76%; $\mathbf{1b}^+$ 100%).

Calculations on model compounds

A theoretical calculation of molecules such as **1a** or **1b** with geometry and energy optimization is prohibitively expensive because of their size and the complete absence of symmetry. We felt, however, that calculation and comparison of simple model compounds such as $HP{=}CH_2$ (**16**) and $HN{=}CH_2$ (**17**) would give sufficiently reliable information; even if absolute values may be somewhat in error, the results are expected to give a qualitatively correct picture of features such as orbital sequence, overlap densities, charge distribution, d-participation etc. In order to make the extrapolation to **1a** and **1b** more realistic, and to check possible conjugative interactions, calculations were also performed on phenyl substituted derivatives of **16**: $PhP{=}CH_2$ (**18**) and E-HP=CHPh (**19**). Finally, E-HP=$CHNMe_2$ (**20**) was included, because, as mentioned before, C-heterosubstituted phospha-alkenes are well known in the literature[2d,8,24] and show a remarkable stability and other properties attributable to the contribution of resonance structures such as **20a**.

The calculations were performed with the LCAO Hartree–Fock–Slater program developed by Baerends and Ros,[25] which has been shown to give results of the same quality as Hartree–Fock results.[26] Double zeta basis sets (STO) were used as reported



20 20a

by Clementi;[27] the exchange scaling parameter α was set at 0.7; the C-$1s^2$, N-$1s^2$ and P-$1s^2 2s^2 2p^6$ cores were kept frozen.

Chronologically, these calculations were performed before the results of the X-ray structure determinations (see next section and Ref. 12*c*) were known. Although variations in bond angles within reasonable limits are expected to have only a small effect on features such as one-electron level spacing etc. we tried to approach the presumable molecular geometries of **1a** and **1b** as much as possible. For this reason, we did not use the experimentally determined structural parameters of **16**.[3] In order to avoid confusion with the "real" **16**, the molecule calculated with our assumed geometry will henceforth be designated as **16'**. In particular, the R–P=C angle was expected (and found for **1a** (R=Mes), *vide infra*) to be larger than 97.5° as found for **16**[3] (R=H); it was chosen to be 120° in analogy with the corresponding angle (120.8°[28]) in **14**, the nitrogen analogue of **1a**. The following assumptions were made: (a) all molecules have C_s symmetry; (b) all bond angles are 120°; (c) the bond lengths are (in Å): C–H 1.09, N–H 1.04, P–H 1.42[3], C–C (phenyl) 1.42, C–Ph 1.50, N–Ph 1.43,[28] P–Ph 1.70, N=C 1.30,[28] P=C 1.67;[3] (d) the benzene ring in **18** is perpendicular to the P=C nodal plane (approximation of the actual conformation of **1a**); (e) the *trans*-benzene ring in **19** is in the nodal plane of the P=C bond (36.6° in **1a**, *vide infra*); (f) for **20** (in Å): =C–N 1.40, Me–N 1.47; in the methyl group C–H 1.10 Å, H–C–H 109.5°.

Some salient results are summarized in Tables 2–4; more data are available in Ref. 29. For comparison, the results for ethylene were calculated with the same method and assumptions yielding $q_C = -0.53$, $q_H = -0.26$, $P_{CC(tot)} = 0.52$; HOMO: π (E = −6.32 eV), LUMO: π^* (E = −0.18 eV). The following conclusions may be drawn.

(1) From Tables 1 and 2 it is apparent that, in line with expectation, the inclusion of d-functions has little influence on the results for **17**; the effect is most pronounced on the Mulliken gross atomic charges *q*, but this may be partly due to the *ad hoc* partition of the overlap density.[29] For this reason, difference density plots (see conclusion 2) in our opinion give a more reliable picture of the bonding situation. It should be mentioned that the first entries in Tables 1 and 2 (without addition of d-functions) are in line with earlier results on **17**.[30]

(2) In order to eliminate artificial effects of the Mulliken population analysis, the redistribution of electrons upon π-bond formation was examined by difference density plots, in which the density of np_z (N, C: n = 2; P: n = 3; each occupied by one electron) is subtracted from the π-density of $HX{=}CH_2$ and plotted on the YZ-plane (perpendicular to the nodal plane of X–C and through X and C). For **17**, the result is presented in Fig. 1(a). It is apparent, as from Table 2, that the π-MO is polarized towards the more electronegative nitrogen atom. The overlap population between N and C is lower than between C and C in ethylene (*vide supra*); this points to less bonding, although a direct correlation between bond strength and overlap population may not be drawn.

(3) Contrary to **17**, were the density difference plot with or without inclusion of d-functions gives essentially the same picture, there is a pronounced difference for the density difference plots of **16'** without (Fig. 1b) and with addition of d-functions (Fig. 1c). This change demonstrates the importance of 3d functions on phosphorus. Although the contribution of P 3d orbitals to the P=C bond is difficult

Table 2. Computed energy levels of **16'** and **17** (−E, in eV)[a]

Compound	formula	1a'	2a'	3a'	4a'	1a"	5a'
17	$HN{=}CH_2$	21.7	14.9	11.7	10.1	7.5	4.5
17[b]		21.2	14.7	11.4	10.2	7.3	4.8
16'	$HP{=}CH_2$	17.8	13.5	10.5	9.7	6.3	4.9
16'[b]		17.4	13.3	10.3	9.5	6.1	5.1

[a] The one-electron energies do not correspond directly with ionisation potentials. A good estimate of the latter may be obtained from the data in the Table by adding a constant value of 4 eV (e.g. for 16', 5a': IP = 9.1 eV).

[b] d-functions added.

Table 3. Computed Mulliken gross atomic charges (q, in Z) and overlap populations (P, in electrons) in **16'** and **17**

Compound	X	q_X	q_C	$q_{H(X)}$	q_{Z-H}	q_{Z-H}	P_{XC} (tot.)	$P_{XC}(\pi)$
17	N	-0.57	-0.32	+0.38	+0.24	+0.27	0.36	0.22
17[a]	N	-0.70	-0.20	+0.40	+0.24	+0.26	0.37	0.23
16'	P	+0.28	-0.91	+0.02	+0.30	+0.32	0.38	0.22
16'[a]	P	-0.31	-0.57	+0.28	+0.29	+0.31	0.52	0.25

[a] d-functions added.

to define unambiguously and quantitatively due to nonuniqueness of basis set expansions of orbitals, the influence of the relatively low-lying P 3d orbitals is undeniable. All further calculations reported here were therefore performed with a diffuse 3d function ($\alpha = 1.20$) added at the phosphorus atom.

(4) While the HOMO in ethylene and **20** is a π-MO, the HOMO in **17**, **16'**, **18** and **19** is a σ-MO, i.e. essentially the lone pair at the hetero atom. For **17**, this is in accord with previous calculations.[30] For **16'** these results are at variance with those of Thomson[31] and those of Schoeller and Niecke[32] who calculated the π-MO to be the HOMO for **16**. There is, however, a difference in geometry, as Schoeller and Niecke used an optimized geometry of **16**, which differs from that of **16'** mainly in the angle C–P–H (97.1° vs 120°). When we changed our angle C–P–H to 97.5°, the π-orbital (1a") was hardly affected, but the phosphorus lone pair orbital (5a') was stabilized and became essentially degenerate with the π-orbital (orbital energies: 1a"–6.2 eV, 5a'–6.1 eV; ionization potentials 10.2 eV and 10.1 eV respectively, see note a in Table 2). In general, HFS calculations with a flexible basis (double zeta or better) give excellent agreement with ionization potentials. We therefore consider it probable that in derivatives of **16** with an angle C–P–R $\geqslant$ 97.5°, such as **1a** (R=Mes), the HOMO is the phosphorus lone pair orbital. It should, however, be pointed out that *all* calculations agree to predict the π and phosphorus lone pair orbitals to be close in energy, and, depending on the reaction partner, both may become important as frontier orbitals.

(5) The calculated dipole moment of **17**

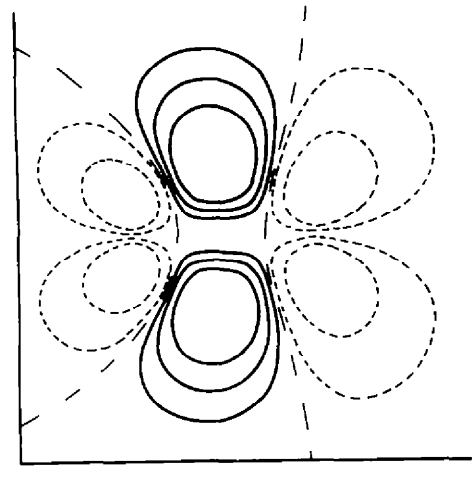
Table 4. Comparison of frontier orbitals: energies (−E, in eV), Mulliken gross atomic charges (q, in Z) and overlap populations (P, in electrons)

Compound	formula	X	π	σ	π^*	q_X	q_C	$P_{XC(tot)}$	$P_{XC(\pi,tot)}$	$P_{XC(\pi)}$[a]
17	$HN{=}CH_2$	N	7.5	4.5	μ	-0.57	-0.32	0.36	0.22	
16'	$HP{=}CH_2$	P	6.1	5.1	2.0	-0.31	-0.57	0.52	0.25	0.25
18	$PhP{=}CH_2$	P	5.7	4.5	1.5	+0.02	-0.51	0.53	0.25	0.20
19	$E{-}HP{=}CHPh$	P	5.4	5.3	2.5	-0.36	-0.29	0.52	0.23	0.13
20[b]	$E{-}HP{=}CHNMe_2$	P	3.8[c]		0.6	-0.45	-0.18	0.49		

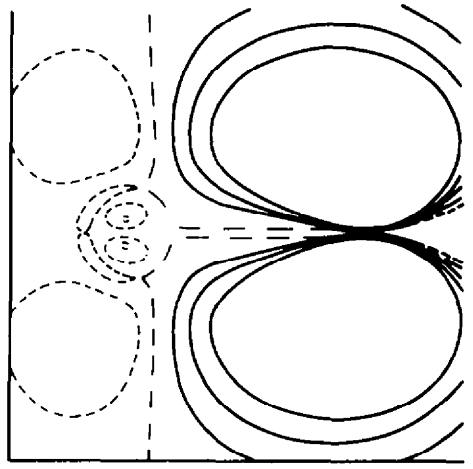
[a] $P_{XC(\pi)}$ indicates the overlap population in the highest π-MO (4th column).

[b] q_N=-0.33, $P_{CN(tot)}$=0.37.

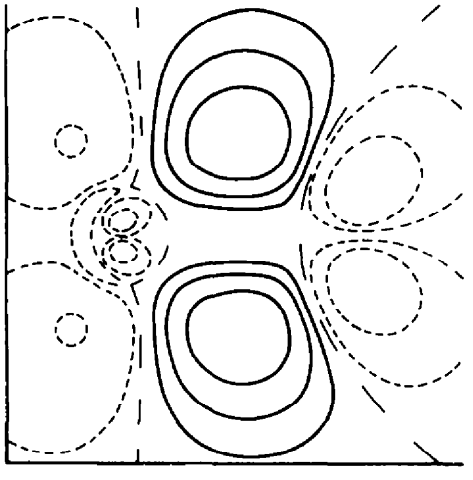
[c] HOMO.



(a)



(b)



(c)

Fig. 1. Difference density plots (π-np_z): (a) for **17**, (b) for **16'** without addition of d-functions; (c) for **16'** with addition of d-functions. The dashed line is the zero contour; the solid lines are positive contours (0.003, 0.006, 0.01); the dotted lines are negative contours (−0.002, −0.01).

(μ = 2.04 D) with nitrogen as the negative pole compares favourably with that calculated by Lehn *et al.* (μ = 2.49 D).[30a] The dipole moment of **16'** (μ = 0.76 D) is less pronounced and has phosphorus as the positive pole; it is in good agreement with the value (μ = 0.869 D) determined from microwave spectroscopy.[30b]

(6) In agreement with experience (previous section), conclusions 4 and 5 predict that **1a** and **1b** on reaction with strongly polar reagents show a regiochemistry controlled by the polarization of the P=C bond (conclusion 5), while "soft" electrophiles will most likely attack at the phosphorus lone pair because of frontier orbital control (conclusion 4). As pointed out before, in such a situation it can be dangerous to predict the regiochemistry, the more so as steric factors may also be of major importance.

(7) In general, the influence of phenyl substituents on phosphorus (**18**) or carbon (**19**) is small (Table 4). This supports our experimentally derived claim that phenyl substitution as such does not significantly change the thermodynamic stability of phosphaethenes.

(8) More in detail, the phenyl group on phosphorus in **18** both increases the positive charge on phosphorus and raises the energy of the σ-HOMO. While the former effect would be expected to stabilize the π-MO by contraction of the 3p-orbitals on phosphorus, the energy of the π-MO is actually slightly higher. The considerable destabilization of the lone pair by the phenyl group may be caused by its perpendicular orientation to the P=C nodal plane; hereby, the phenyl-π-system interacts with the lone pair.

(9) With regard to **20**, the data of Table 4 point to a considerable contribution of structure **20a**. This is deduced from (a) the decreased overlap population P_{PC} (b) from P_{CN} which is rather high compared to normal N–C(sp^3) populations, and (c) from the more negative charge on phosphorus. Even though this resonance is less favourable for electronegativity reasons, as negative charge is conferred from nitrogen to phosphorus, this effect is apparently overruled by the more favourable π-overlap between N and C ($2p\pi$–$2p\pi$) than between P and C ($3p\pi$–$2p\pi$). This conclusion endorses our hypothesis that C-heterosubstituted phospha-alkenes are thermodynamically stabilized by reasonance such as **20**↔**20a**.

(10) We calculated the n→π^* transition in **16'** to occur at 352 nm, which is in reasonable agreement with the observed values for **1a** (λ_{max} = 324 nm) and **1b** (λ_{max} = 322 nm).

The crystal and molecular structure of **1a**

For a completely novel class of compounds such as the stable phospha-alkanes, it was desirable to obtain exact structural information, in particular with respect to the geometry around the P=C bond. Therefore, the X-ray structure determination of **1a** was undertaken. Selected data of the structure have been published in a preliminary form.[19]

Crystals of **1a** are monoclinic, space group $P2_1/c$ with 4 molecules in a unit cell of dimensions a = 11.938(2), b = 6.382(2), c = 23.66(2) Å and β = 90.81(2)°. A total of 2420 reflections with $\theta < 65°$ were measured on a NONIUS CAD 4 diffractometer

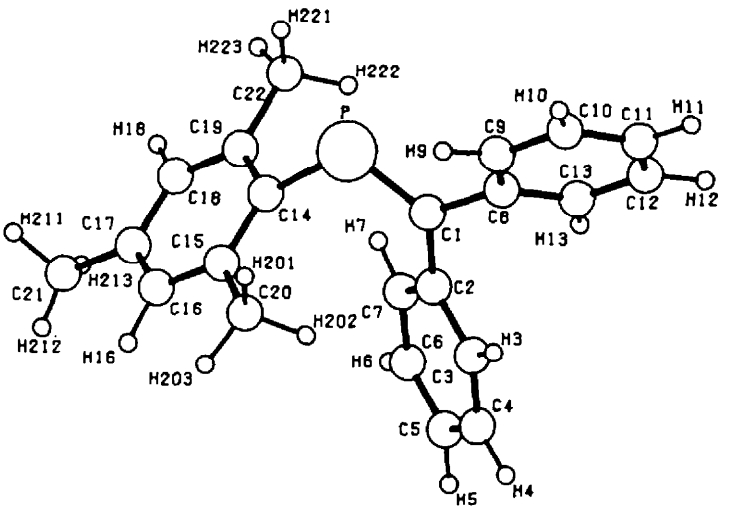


Fig. 2. PLUTO drawing of **1a** and atom numbering.

using graphite monochromated CuKα radiation. No absorption correction was applied.

The structure was completely solved from an E^2-Patterson synthesis. Refinement proceeded by means of anisotropic block-diagonal least-squares calculations. Towards the end of the refinement a ΔF-synthesis revealed the hydrogen atoms except those of methyl groups. The former were introduced with isotropic temperature parameters, the latter were kept fixed at their calculated positions. The final R value was 0.054. A weighting scheme $w = 1/(0.4 + F_o + 0.007 \times F_o^2)$ was used and the anomalous scattering of P was taken into account. The results are presented in Tables 5–10 (deposited with the Cambridge Crystallographic Data Centre).

The P=C group in **1a** has the geometry expected for a "genuine" phosphorus-carbon double bond. Within the limits of accuracy, its σ-skeleton is planar (cf. Table 9: plane I through PC(1)C(2)C(8)C(14)). The P=C bond length of 1.692(3) Å approaches that of $HP{=}CH_2$ (**16**)[3] (1.67 Å) and is clearly shorter than that of a P–C single bond (1.87 Å)[34] or even that in delocalized system (1.72–1.80 Å).[2,35] In fact, the data for localized P=C bonds known so far confirm the rule for other element-carbon double bonds such as C=C, N=C, O=C: the difference between the lengths of the E–C single bond and the E=C double bond is constant and about 0.20 Å.[34] It has been pointed out that for benzene and Group 5 heterobenzenes, the difference between the bond lengths of the E–C single bond and the *delocalized* E···C bond in the aromatic ring is also nearly constant; expectedly, it has the smaller value of 0.13–0.15 Å.[2c] From the linear correlation between carbon-carbon and carbon-phosphorus (multiple) bond lengths, a radius of 1.00 Å has been derived for sp^2-hybridized phosphorus.[3b] Although the accuracy of the present structure determination should not be overemphasized, a slightly larger radius (1.02 Å) seems to be indicated for **1a**. This may be due either to a slight antibonding interaction with the phenyl group, as discussed in the previous section, or to a non-symmetrical distribution of s- and p-character over the lone pair and the P–C(1) and P–C(14) bonds (*vide infra*).

The mesityl ring (plane II in Tables 9 and 10) forms a dihedral angle of 71° with the P=C nodal plane; this excludes significant resonance interaction between the two systems. The phenyl groups at C(1) form smaller angles with the P=C plane, the magnitude of which is apparently governed by Van der Waals interactions (Table 10: Z–Ph (plane III) 42.9°; E–Ph (plane IV) 36.6°), although crystal packing effects may also play a role in the solid state. For such intermediate angles conjugative interaction with the P=C π-system cannot be fully excluded; the C(1)-phenyl bond lengths (*ca.* 1.49 Å°) are not distinctive, because they are normal for $C(sp^2)$–$C(sp^2)$ bonds both with[37] or without[38] π-conjugation across this bond. Van der Waals interaction is probably responsible for the widening of the angle involving the Z-phenyl group (P–C(1)–C(2), 127.2°) as compared to the E-phenyl group (P–C(1)–C(8), 116.2°).

It is of interest to compare the structure of **1a** with those of its metal complexes.[12b–d] In general, the congruence in geometric features of **1a** as such and as a ligand is surprisingly close, in particular for **1a** and its $Cr(CO)_5$-complex;[12c] for Pt(0)[12d] and Pt(II),[12b] the deviations are larger, but not dramatic and may in part be of steric origin. A similar congruence of structures for the free and complexed ligand had earlier been observed for an aminoiminophosphine.[39] In these cases, complexation to the metal centre via the phosphorus lone pair apparently causes no gross disturbances in the rest of the molecule. The more subtle differences in structure and other aspects of the coordination chemistry of phospha-alkenes will be discussed in a forthcomming paper.

Informative also is the comparison of the structure of **1a** with that of its unsubstituted parent compound **16**[3b] and with its nitrogen analogue **14**[28]. Most conspicuous are the different bond angles at the heteroatom, i.e. H–P=C (97.5°), Mes–P=C (107.5°) and Mes–N=C (120.8°). While the nearly ideal sp^2-angle at nitrogen clearly reflects the hybridization of this

first Row element, the small angle in **16** is usually explained by invoking $sp^n(n > 2)$ hybridization of phosphorus in the P–H and/or P–C bond (and consequently higher s-character in the lone pair). The reason for the opening of this angle from **16** to **1a** is not quite clear at the moment. It seems too large to be purely steric of origin; an electronegativity argument (Bent's rule[40]) would even predict the opposite effect for replacing PH by PMes. It is also remarkable—as previously discussed for the $Cr(CO)_5$-complex of **1a**[12c]—that the P-aryl bond lengths is practically identical in **1a** (1.828(3) Å) and in triphenylphosphine (1.822 Å).[41] Again, it seems that the simple sp^2-description for **1a** is not adequate. Possibly, the identity of the two bond lengths is coincidental and results from two or several factors working in opposite directions in the two compounds. For instance, slightly increased p-character (compared to sp^2) in the P–Mes bond in **1a** might cause elongation, while in triphenylphosphine, a certain degree of conjugation would lead to contraction of the P–Ph bond.

CONCLUSION

The triarylphospha-alkenes **1a** and **1b** have been obtained by elimination of HCl from the precursors **11** (Scheme 1). This synthetic approach to phospha-alkenes appears to be the most general and useful one, even though several other strategies for the construction of the P=C function are available and may be advantageous in specific cases.[2d]

The crystal and molecular structure of **1a**, the chemical and physical properties of **1a** and **1b**, and HFS-calculations on simple models lead to a consistent description of these molecules as "genuine" phospha-alkenes having a P=C double bond which, comparable to double bonds between First Row elements, is composed of σ- and π-components. However, the P=C bond is thermodynamically and kinetically less stable than a N=C or C=C bond. Therefore, phospha-alkenes which are not stabilized by conjugation, in particular by heteroatoms, are not isolable under ordinary conditions unless stabilized by steric protection of the P=C bond as in **1a** and **1b**.

EXPERIMENTAL

NMR spectra were recorded on a Bruker WH 90 or a WM 250 spectrometer. A positive sign of a chemical shift indicates a downfield shift relative to H_3PO_4 (external for ^{31}P) or tetramethylsilane (internal for ^1H and ^{13}C). IR spectra were recorded on a Perkin–Elmer 237, a Hitachi 124 and a Beckman 580 B spectrometer. UV spectra were obtained with a Perkin–Elmer 137 and a Cary 118 spectrometer. Reactions were performed under an argon or nitrogen atmosphere; small scale runs were performed in sealed, evacuated systems. Solvents are distilled from lithium aluminum hydride under an inert atmosphere prior to use. Melting points are uncorrected. Elemental analyses were performed by Organisch Chemisch Instituut TNO, Zeist.

2,4,6-Trimethylphenyl(diphenylmethylene)phosphine **1a**

Compound **11a** (4.4 g, 12.5 mmol) was dissolved in THF (150 mL) and DBU (3.0 g, 20 mmol) was added dropwise at room temperature under stirring. Stirring was continued for another 2.5 h, and after 20 h the white precipitate was filtered off, and washed with cyclohexane (20 mL). After evaporation of the filtrate, a dark yellow oil (6.2 g) was obtained. This oil was dissolved in cyclohexane (50 mL); the solution was filtered and the filtrate evaporated. A yellow oil (5.0 g) remained. This oil was distilled (140°, 10^{-3} mbar) to give **1a** (2.5 g, 7.9 mmol, 63%) as a yellow oil. Crystallization from cyclohexane in a sealed and evacuated vacuum system gave yellow transparant crystals, m.p. 83–85°. ^1H NMR ($CDCl_3$): $\delta = 2.19$ (s, 3H, *p*–CH_3), 2.27 (s, 6H, *o*–CH_3), 6.69 (s, 2H, Mes H), 6.75–7.60 (m, 10H, aryl H). ^{13}C NMR ($CDCl_3$): $\delta = 21.0$ (s, *p*–CH_3), 22.1 (d, $^3J_{PC} = 9$, *o*–CH_3), 125.5–144.9 (m, aryl C), 193.4 (d, $^1J_{PC} = 43.5$, P=C). ^{31}P NMR ($CDCl_3$): 233. Mass spectrum *m/z* (relative intensity) 316 (76) M^+, 301 (4) $[M–Me]^+$, 270 (41.5), $[M–Me–P]^+$, 167 (100) $[Ph_2CH]^+$. Exact mass *m/z* 316.1388 (Calc for $C_{22}H_{21}P^+$, *m/z* 316.1381). IR (CCl_4, cm^{-1}): 3000–2900 (C–H), 1600 (C=C, aromatic) 1490, 1445 (P–Ph),917 (P=C), 850, 690 (C–H, Ph). UV: see Table 1. Found: C, 82.58; H, 6.80 $C_{22}H_{21}$ P (M = 316.36) requires: C, 83,52; H, 6.69%.

2,6-Dimethylphenyl(diphenylmethylene)phosphine **1b**

Compound **11b** (54.6 g, 161 mmol) was dissolved in THF (600 mL) and DBU (27.7 g, 182 mmol) in THF (50 mL) was added dropwise at room temperature. A white precipitate was formed. After stirring for 1 h, the solution was filtered and the filtrate evaporated. Pentane (350 mL) was added; a white precipitate was formed and filtered off. Evaporation of the filtrate gave a yellow/green oil of **1b** (44.5 g, 92%), which solidified slowly at room temperature. Further purification could be achieved by column chromatography as follows: kieselgel (35–70 mesh) was eluted with anhydrous diethyl ether prior to use under an atmosphere of nitrogen; **1b** was obtained by elution with diethyl ether as a yellow/green oil, (40.0 g, 83%), which solidified completely on standing, m.p. 75.5–80°. ^1H NMR ($CDCl_3$): $\delta = 2.32$ (s, 6H, *o*–CH_3), 6.77–7.66 (m, 13H, aryl H). ^{31}P NMR ($CDCl_3$): $\delta = 232.5$. ^{13}C NMR ($CDCl_3$): $\delta = 22.2$ (d, $^3J_{PC} = 7.4$, *o*–CH_3) 125.8–145.1 (m, aryl C), 193.6 (d, $^1J_{PC} = 42.4$, P=C). IR (CCl_4, cm^{-1}): 3060, 3030 (C–H, unsaturated). 2940 (C–H, saturated), 1600 (C=C, aromatic), 1490, 1450 (P–Ph), 910 (P=C), 690 (C–H, Ph). Mass spectrum *m/z* (relative intensity) 302 (100) M^+, 287 (4) $[M–Me]^+$ 224 (20), 167 (37) $[Ph_2CH]^+$, 152 (12), 105 (14) $(M–PCPh_2]^+$. Exact mass *m/z* 302.1220 (Calc for $C_{21}H_{19}P^+$ *m/z* 302.1224). Found: C, 83.70, 82.28; H, 6.23, 6.58; P, 9.96, 10.45. $C_{21}H_{19}P$ (M = 302.33) requires: C, 83.42; H, 6.33; P, 10.24%.

Bis(diethylamino)-2,4,6-trimethylphenylphosphine **7a**

2,4,6-Trimethylphenylmagnesium bromide **5a** (0.29 mol, prepared from 2,4,6-trimethylbromobenzene (67.6 g, 0.34 mol) and magnesium (10 g, 0.41 mol) in THF (105 mL) was added dropwise under stirring to a solution of **6a** (61.5, 0.29 mol) in THF (50 mL) at −40 to −50°. The mixture was stirred for 1.5 h. The solution was filtered and the precipitate extracted once with THF (50 mL). The filtrate was evaporated and the crude residue was extracted twice with pentane (300 and 50 mL, respectively) and the extracts were evaporated. **7a** remained as a yellow oil (74.5 g, 87%). ^1H NMR ($CDCl_3$): δ 1.04 (t, $^3J_{HH} = 7$, 12 H, CH_2CH_3), 1.12 (s, 3H, *p*–Me), 2.44 (s, 6H, *o*–Me), 2.98 (d of q, $^3J_{PH} = 9$, $^3J_{HH} = 7$, 8H, CH_2CH_3).

Bis(diethylamino)-2,6-dimethylphenylphosphine **7b**

2,6-Dimethylphenylmagnesium bromide (**5b**) (89 mmol, prepared from 2,6-dimethylbromobenzene (17.2 g, 93 mmol) and magnesium (7 g, 291 mmol) in THF (190 mL)) was added dropwise under stirring to a solution of **6**[42] (18.8 g, 89 mmol) in THF (50 mL) at −55 to −70°. The mixture was stirred for 2 h and after standing for 20 h at room temperature, the solution was filtered. The precipitate was extracted once with THF (20 mL). The filtrate was evaporated and the crude residue was extracted twice with pentane (90 and 20 mL, respectively) and the extracts were evaporated. Pure **7b** (22.9 g, 92%) remained as a yellow oil. ^1H NMR ($CDCl_3$): $\delta = 1.04$ (t, $^3J_{HH} = 7$, 12 H, CH_2CH_3),

2.44 (d, $^4J_{PH}$ = 1.5, 6H, *o*–CH_3), 2.99 (d of q, $^3J_{HH}$ = 7, $^3J_{PH}$ = 8.5, 8H, CH_2CH$_3$), 6.78–7.00 (m, 3H, aryl H).

Dichloro-2,6-dimethylphenylphosphine **8b**

A solution of 2,6-dimethylphenylmagnesium bromide (**5b**) (0.18 mol, prepared from 2,6-dimethylbromobenzene (36.5 g, 0.20 mol) and magnesium (5 g, 0.21 mol) in THF (150 mL)) was added under stirring at −80° to the solution of **6**[42] (0.18 mol) in THF; after addition the solution was stirred for 1 h at room temperature. The reaction mixture was filtered and the filtrate evaporated. The residue was dissolved in cyclohexane (250 mL) and HCl gas bubbled through for 2.5 h. After filtration and evaporation of the solvent the residue was distilled, yielding a colourless oil of **8b** (11.2 g, 30%; b.p. 80–90°, 1 mbar).^{1}H NMR (CDCl$_3$): δ = 2.73 (d, $^4J_{PH}$ = 4, 6H, Me), 6.93–7.40 (m, 3H, aryl H). ^{31}P NMR (CDCl$_3$): δ = 167.

Diethylaminochloro-2,4,6-trimethylphenylphosphine **9a**

(a) *From* **4a** *directly*. A solution of the Grignard reagent **5a** (0.6 mol) from **4a** in THF (600 mL) was added dropwise to the solution of **6**[42] (126.3 g, 0.6 mol) in diethyl ether (700 mL) at 0° under stirring. The reaction mixture was stirred for 1 h at room temperature and allowed to stand overnight. After filtration, HCl gas was bubbled through the filtrate until the ^{1}H NMR spectrum of a sample indicated the complete conversion of **7a** to **9a**; the solution was then filtered and the filtrate evaporated to dryness. The residue was extracted with cyclohexane, and after evaporation of the cyclohexane, the residue was distilled, yielding a colourless oil of **9a** (83.5 g, 54%; b.p. 120°, 10^{-1} mbar).

(b) *From* **7a**. **7a** (74.5 g, 0.25 mol) was dissolved in diethyl ether (150 mL). Hydrogen chloride (320 mL of a 1.68 N solution in diethyl ether) was added in several portions until ^{1}H NMR spectra of a sample indicated that the reaction was completed. The solution was filtered and the filtrate evaporated. The crude residue (54 g) was distilled and gave **9a** (31.4 g, 49%; b.p. 130°, 10^{-3} mbar). ^{1}H NMR (CDCl$_3$): 6.91 (d, $^4J_{PH}$ = 3, 2H, aryl H), 3.20 (d of q, $^3J_{HH}$ = 7, $^3J_{PH}$ = 11, 4H, CH_2CH$_3$), 2.63 (d, $^4J_{PH}$ = 3, 6H, *o*–Me), 2.29 (s, 3H, *p*–Me), 1.11 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3).

Diethylaminochloro-2,6-dimethylphenylphosphine **9b**

7b (21.1 g, 75 mmol) was dissolved in diethyl ether and phosphorus trichloride (5.2 g, 37.8 mmol) dissolved in ether (25 mL) was added dropwise under stirring. After stirring for 3 h the white/orange precipitate was filtered off, and the filtrate was evaporated. The residue (23.4 g) was distilled yielding **9b** as a colourless oil (15.8 g, 87%; b.p. 103°, 10^{-3} mbar). ^{1}H NMR (CDCl$_3$): δ = 1.11 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3), 2.64 (d, $^4J_{PH}$ = 3, 6H, *o*–Me), 2.78–3.44 (m, 4H, CH_2CH$_3$), 6.78–7.38 (m, 3H, aryl H). ^{31}P NMR (CDCl$_3$): δ = 142.1.

Diethylaminochloro-2-methylphenylphosphine **9c**

As described for **9a**, procedure (a), **9c** was obtained from 0.6 mol **5c**. Distillation yielded a colourless oil of **9c** (70.2 g, 51%; b.p. 90–93°, 10^{-3} mbar). ^{1}H NMR (CDCl$_3$): δ = 1.03 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3), 2.45 (s, 3H, *o*–Me), 3.02 (d of q, $^3J_{HH}$ = 7, $^3J_{PH}$ = 12, 4H, CH_2CH$_3$), 7.0–8.3 (m, 4H, aryl H).

Diethylamino(diphenylmethyl) - 2, 4, 6 - trimethylphenylphosphine **10a**

To a solution of **9a** (54.1 g, 0.21 mol) in diethyl ether, at 0° a solution of α-lithiodiphenylmethane (prepared from diphenylmethane (35.3 g, 0.21 mol)) in THF (300 mL) and n-butyllithium (160 mL of a 1.5 N solution in hexane) was added dropwise under stirring. After standing for 20 h at room temperature the solution was filtered and evaporated; the residue was distilled. This distillation needs to be carried out fast, with a very short vigreux column and the oil bath heated to the required temperature before immersing the distillation flask; otherwise **10a** is obtained in poor yield and is contaminated by diphenylmethane. **10a** (53.9 g, 66%) was obtained as a yellow liquid (b.p. 170–180°, 10^{-3} mbar). ^{1}H NMR (CDCl$_3$): δ = 0.59 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3), 2.17 (s, 3H, *p*–Me), 2.51 (d, $^4J_{PH}$ = 2, 6H, *o*–Me), 2.83 (d of q, $^3J_{HH}$ = 7, $^3J_{PH}$ = 7.5, 4H, CH_2CH$_3$), 5.20 (s, 1H, methine H), 6.67 (d, $^4J_{PH}$ = 2, 2H, P-aryl H), 7.04–7.64 (m, 10H, Ph H). ^{31}P NMR (CDCl$_3$): δ = 64.5. Mass spectrum *m/z* (relative intensity): 389 (1) M^+, 317 (2) $[M–Et_2N]^+$, 222 (100) $[M–Ph_2CH]^+$.

Diethylamino(diphenylmethyl)-2,6-dimethylphenylphosphine **10b**

Benzhydryl ethyl ether (24.3 g, 115 mol) was added dropwise to a suspension of a sodium–potassium alloy (Na: 2.4 g, K: 10.1 g) in THF (450 mL). The mixture became warm and deep red. After 30 min the reaction mixture was centrifuged and the supernatant solution was decanted. It was added dropwise to **9b** (25.45 g, 105 mol) (75 mL) at −60° under stirring. After slowly warming to room temperature and standing for 20 h, the solution was dark red/brown. Methanol (1 mL) was added to destroy small amounts of excess diphenylmethyl potassium. After standing for another 96 h, a white precipitate was removed from the orange/yellow solution by centrifugation and decantation. The residue was extracted by stirring in THF (100 mL) and centrifugation. The combined solutions were evaporated. The brown residue was purified by column chromatography on silicagel (35–70 mesh) and elution with diethyl ether; prior to use, the contents of the column was dried by washing with anhydrous diethyl ether; **10b** (37.5 g, 97%) was obtained after evaporation of the solvent as a yellow oil, which solidified on standing; ^{1}H NMR (CDCl$_3$): δ = 0.56 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3), 2.51 (d, $^4J_{PH}$ = 1, 6H, *o*–Me), 2.80 (d of q, $^3J_{HH}$ = 7, $^3J_{PH}$ = 7, 4H, CH_2CH$_3$), 5.15 (s, 1H, methine H), 6.66–7.56 (m, 13H, aryl H).

Diethylamino(diphenylmethyl)-2-methylphenylphosphine **10c**

As described for **10a**, **10c** was prepared from **9c** (48.2 g, 0.21 mol) by reaction with α-lithiodiphenylmethane (0.21 mol). Rapid distillation (*cf* **10a**) yielded a colourless oil of **10c** (48.1 g, 63%; b.p. 150–160°, 10^{-3} mbar). ^{1}H NMR (CDCl$_3$): 0.48 (t, $^3J_{HH}$ = 7, 6H, CH$_2$CH_3), 2.50 (s, 3H, *o*-Me), 2.77 (d of q, $^3J_{PH}$ = 7, $^3J_{HH}$ = 7, 4H, CH_2CH$_3$), 4.80 (d, $^2J_{PH}$ = 3, methine H), 6.80–7.57 (m, 14H, aryl H)

Diethylamino(diphenylmethyl)phenylphosphine **10d**

As described for **10a**, **10d** was prepared from **9d**[43] (72.9 g, 0.34 mol) by reaction with α-lithiodiphenylmethane (0.34 mol). On attempted distillation, **10d** polymerized. As it was nearly 100% pure according to the ^{1}HNMR spectrum, **10d** was used for the attempted conversion to **1d** without further purification. ^{1}H NMR (CDCl$_3$): 0.66 (t, $^3J_{HH}$ = 6, 6H, CH$_2$CH_3), 2.84 (d of q, $^3J_{PH}$ = 7, $^3J_{HH}$ = 6, 4H, CH_2CH$_3$), 4.73 (d, $^2J_{PH}$ = 4, 1H, methine H), 6.91–7.69 (m, 15H, aryl H).

Chloro(diphenylmethyl)-2,4,6-trimethylphenylphosphine **11a**

To a solution of **10a** (25.6 g, 65.8 mmol) in diethyl ether (450 mL), a solution of HCl in THF (70 mL, 2.14 N) was added dropwise under stirring; the progress of the reaction was monitored by measuring the ^{1}H NMR spectrum of samples. The solution was filtered and evaporated. The residue was extracted with cyclohexane; after filtration, the filtrate was evaporated. A ^{1}H NMR spectrum of the remaining yellow oil (16.8 g) showed besides **11a** (73% according to the integral of the methine proton and the aromatic protons) diphenylmethane and unidentified compounds. The procedure described for the preparation of **11b** can also be applied to **11a** and gives a purer product. Attempts to purify **11a** by distillation or sublimation failed, due to partial decomposition. **11a** Could be obtained pure by crystallization from cyclohexane, m.p. 70–79°. ^{1}H NMR (CDCl$_3$): δ = 2.16 (s, 3H, *p*-Me), 2.47 (d, $^4J_{PH}$ = 2, 6H, *o*-Me), 5.27 (s, 1H, methine H), 6.70 (d, $^4J_{PH}$ = 2, 2H, Mes

H), 6.95–7.69 (m, 10H, aryl H). ^{13}C NMR ($CDCl_3$): $\delta = 21.0$ (s, *p*-Me), 22.6 (d, $^3J_{PC} = 20.5$, *o*-Me), 54.5 (d, $^1J_{PC} = 35.2$, methine C), 125.7–144.7 (m, aryl C). ^{31}P NMR ($CDCl_3$): $\delta = 81.4$. Mass spectrum: *m/z* (relative intensity 354 (0.25), 352 (1) M^+, 317 (2) $[M-Cl]^+$, 302 (4), 167 (100) Ph_2CH^+, 165 (67), 119 (40) $[C_9H_{11}]^+$.

Chloro(diphenylmethyl)-2,6-dimethylphenylphosphine **11b**

To a solution of **10b** (37.5 g, 100 mmol) in diethyl ether (350 mL), a solution of phosphorus trichloride (18.8 g, 137 mmol) in diethyl ether (70 mL) was added dropwise. A small amount of white precipitate appeared in solution. After evaporation of the reaction mixture, the oily yellow residue was dissolved in pentane (200 mL); after 20 h white needless of **11b** separated (14.8 g; m.p. 103–106°). A second fraction of **11b** was obtained after concentration of the mother liquor (5.8 g), and a third fraction (3.1 g) by distilling off the volatile constituents (pentane, diethylaminodichlorophosphine) under reduced pressure (24°, 10^{-3} mbar). Total yield of **11b**: 23.7 g, 70%. ^1H NMR ($CDCl_3$): $\delta = 2.52$ (d, $^4J_{PH} = 2$, 6H, *o*-Me), 5.27 (s, 1H, methine H), 6.66–7.77 (m, 13H, aryl H). ^{31}P NMR ($CDCl_3$): $\delta = 81.2$. Mass spectrum *m/z* (relative intensity) 340 (0.25), 338 (1.3) M^+, 303 (2) $[M-Cl]^+$, 168 (49), 167 (100), 166 (23.6) $[Ph_2CH^+]$ 165 (64), 152 (35). Exact mass *m/z* 338.0991 (Calc for $C_{21}H_{20}ClP^+$, *m/z* 338.0988. Found: C, 74.29; H, 6.21; Cl, 9.85; P, 9.18. $C_{21}H_{20}ClP$ (M = 338.79) requires: C, 74.44; H, 5.95; Cl, 10.46; P, 9.14%.

Chloro(diphenylmethyl)-2-methylphenyl phosphine **11c**

A solution of HCl (0.28 mol) in THF (50 mL) was added dropwise to a solution of **10c** (50.5 g, 0.14 mol) in THF (400 mL) at 0°. The solution was stirred at room temperature for 1 h, then filtered and the filtrate evaporated; the residue was distilled and yielded **11c** (40.9 g, 90%; b.p. 200°, 10^{-3} mbar) as a colourless oil. ^1H NMR ($CDCl_3$): $\delta = 1.97$ (d, $^4J_{PH} = 2$, 3H, Me), 4.52 (s, 1H, methine H), 6.82–8.04 (m, 14H, aryl H).

Chloro(diphenylmethyl)-2-methylphenylphosphine **11c**

As described for **11c**, **11d** was prepared from **10d** (48.6 g, 0.14 mol) and HCl (0.28 mol). Sublimation yielded white crystals of **11d** (40.4 g, 93%; sublimed at a bath temperature of 80–90° at 10^{-3} mbar; m.p. 90–93°). ^1H NMR ($CDCl_3$): $\delta = 4.49$ (s, 1H, methine H), 6.89–7.78 (m, 15H, aryl H). Mass spectrum *m/z* (relative intensity) 310 (0.1) M^+, 275 (0.1), 167 (100) $[Ph_2CH]^+$, 165 (29), 152 (16). Exact mass *m/z* 310.0699 (calc for $C_{19}H_{16}ClP$, *m/z* 310.0678).

Diphenylmethyl-2,4,6-trimethylphenylphosphinic chloride **12**

To a solution of **11a** (1 g, 2.7 mmol) in acetone an excess of H_2O_2 was added. After evaporation of the reaction mixture, the residue was crystallized from methanol to yield colourless crystals of **12** (m.p. 160.5–161.5°). ^1H NMR ($CDCl_3$): $\delta = 2.26$ (s, 3H, *p*-Me), 2.59 (s, 6H, *o*-Me), 4.94 (d, $^2J_{PH} = 12$, 1H, methine H), 6.86 (d, $^4J_{PH} = 5$, 2H, Mes H), 7.10–7.88 (m, 10H, aryl H). ^{31}P NMR ($CDCl_3$): $\delta = 53.5$. Found: C, 71.80; H, 6.10. $C_{22}H_{22}ClOP$ (M = 368.82) requires: C, 71.64; H, 6.01%.

1,1-*Diphenyl-2-(2,4,6-trimethylphenyl)ethene* **15**

A solution of diphenylacetaldehyde (5 g, 25.5 mmol) in diethyl ether (50 mL) was added dropwise at room temperature to a solution of **5a** (25.5 mmol, prepared from **4a** (10 g, 50 mmol) and magnesium (1.34 g, 55 mmol) in diethyl ether (100 mL)). The reaction mixture was heated under reflux for 3 h. After cooling to room temperature, a solution of NH_4Cl (5 g, 93 mmol) in H_2O (100 mL) was added. The two layers were separated and the water layer was extracted twice with diethyl ether (20 mL). The combined ether fractions were dried (Na_2SO_4) and evaporated. The oily residue was dissolved in acetic acid (50 mL); a few drops of conc. H_2SO_4 were added, and the mixture was heated at 110° for 1 h. Then the acetic acid was evaporated and the residue was dissolved in toluene and water (1:1). The organic layer was separated, washed with aqueous $NaHCO_3$ solution and H_2O, dried (Na_2SO_4) and evaporated. The oily residue was crystallized from methanol to give **15** (4.7 g, 15.8 mmol, 61.9%), m.p. 70–72.5°. ^1H NMR ($CDCl_3$): $\delta = 2.06$ (s, 6H, *o*-Me), 2.24 (s, 3H, *p*-Me), 6.74 (s, 2H, Mes H), 6.79 (s, 1H, olefinic H), 6.88–7.23 (m, 5H, Ph H), 7.34 (bs, 5H, Ph H). ^{13}C NMR ($CDCl_3$): $\delta = 20.4$ (*o*-Me), 20.9 (*p*-Me), 133.8 (olefinic quarternary C), 127–144.1 (olefinic C(H) + aryl C). Mass spectrum *m/z* (relative intensity) 298 (100) M^+, 283 (26) $[M-Me]^+$, 220 (11), 207 (47), 192 (47). IR spectrum (CCl_4, cm^{-1}) 3075–2900 (C–H), 1605 (C=C aromatic), 1595 (C=C aromatic), 690 (Ph). UV spectrum (THF): λ in nm (log ϵ) 267 (3.06), 273 sh (3.02), 290 sh (2.70). Found: C, 92.42; H, 7.29. $C_{23}H_{22}$ (M = 298.43) requires: C, 92.57; H, 7.43%. On ozonolysis, **15** gave 2,4,6-trimethylbenzaldehyde and benzophenone (^1H NMR and GCMS).

2, 4, 6 - *trimethylphenyl(diphenylmethylene - ^{13}C)phosphine* **1a**-^{13}Ç.

Using common procedures, diphenylmethane-α-^{13}Ç was prepared by the sequence

$$Ba^{13}CO_3 \xrightarrow{H_2SO_4} {}^{13}CO_2 \xrightarrow[2.)H_2O]{1.)PhMgBr} Ph^{13}COOH \xrightarrow{SOCl_2}$$

$$Ph^{13}COCl \xrightarrow[AlCl_3]{C_6H_6} Ph^{13}COPh \xrightarrow[P]{HI} Ph^{13}CH_2Ph.$$

The labelled diphenylmethane was converted to **1a**-^{13}Ç via **10a**-^{13}Ç (^1H NMR ($CDCl_3$): $\delta = 5.20$ (d, $^1J_{CH} = 130$, 1H, methine H; *cf* **10a**)] and **11a**-^{13}Ç [^1H NMR ($CDCl_3$): $\delta = 5.27$ (d, $^1J_{CH} = 135$, 1H, methine H)] as described for the unlabelled compounds. **1a**-^{13}Ç: b.p. 130–140° (10^{-3} mbar). ^1H NMR ($CDCl_3$): identical to that of **1a**. ^{13}C NMR ($CDCl_3$): strongly enhanced signal at $\delta = 193.4$ (d, $^1J_{PC} = 43$). IR of a sample contaminated with DBU (CCl_4, cm^{-1}): 907. Mass spectrum *m/z* (relative intensity) 317 (100 M^+, 302 (5)$[M-Me]^+$, 240 (23), 168 (97) $[Ph_2{}^{13}CH]^+$. Exact mass *m/z* 317.1414 (Calc for $^{12}C_{21}{}^{13}CH_{21}P^+$, *m/z* 317.1400.

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