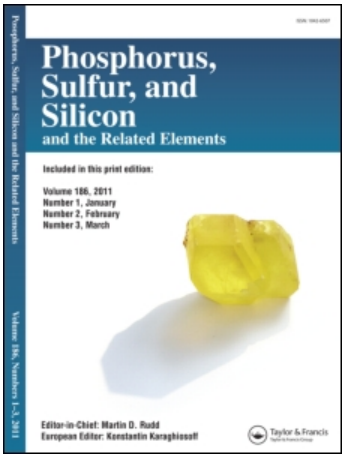

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ATTEMPTED SYNTHESIS OF TRIMESITYLPHOSPHAETHENE; OBSERVATIONS RELATED TO THE MECHANISM OF ACID CATALYZED NUCLEOPHILIC SUBSTITUTIONS AT PHOSPHORUS (III)

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ATTEMPTED SYNTHESIS OF TRIMESITYL-PHOSPHAETHENE; OBSERVATIONS RELATED TO THE MECHANISM OF ACID CATALYZED NUCLEOPHILIC SUBSTITUTIONS AT PHOSPHORUS (III)

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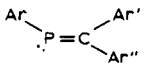
Trimesitylphosphaethene ($MesP{=}CMes_2$, **1f**) is of interest as a sterically protected and presumably very stable phosphaalkene. Its synthesis was attempted along three different routes. The first two routes were modelled after the well-documented syntheses by phosphaalkenes by base catalyzed elimination of hydrogen chloride from $MesPClCHMes_2$ (**3**). In the first approach, **3** could not be obtained from the precursor $MesP(NEt_2)CHMes_2$ (**4**) by treatment with hydrogen chloride. Instead, the phosphonium salt $[MesPH(NEt_2)CHMes_2]^{\oplus}Cl^{\ominus}$ (**2**) was formed; (**2**) is of interest as a "frozen" intermediate in the acid catalyzed nucleophilic substitution at phosphorus(III). The mechanistic implications of its formation and the reasons for its lack of reactivity are discussed.

In the second approach, **3** was obtained from the reaction of $MesPCl_2$ (**8**) with α-potassiodimesitylmethane. However, several attempts to eliminate hydrogen chloride from **3** were unsuccessful. Similarly, the third route, aimed at the preparation of $ClP{=}CMes_2$ (**9**) from $Cl_2PCHMes_2$ (**10**) was thwarted because hydrogen chloride could not be eliminated from **10**. The unusual behavior of **2**, **3**, and **10** can be explained by steric hindrance in these extremely crowded molecules.

INTRODUCTION

Steric protection of the inherently reactive phosphorus–carbon double bond is the most important factor determining the stability of triaryl-substituted phosphaalkenes **1**. For instance, both *ortho*-methyl substituents are required at the P-aryl group in order to obtain thermally stable compounds (**1a**, **1b**);[1] with only one or no *ortho*-methyl substituent (**1c**[1] and **1d**,[1,2] respectively), the triarylphosphaethenes are not stable at room temperature. Similarly, decrease of steric hindrance at the carbon atom of the P=C bond, achieved by forcing the two phenyl rings into one plane as a fluorene moiety, resulted in decreased thermal stability in **1e**.[3]



1

a: Ar = Mes, Ar′ = Ar″ = Ph

b: Ar = 2,6-$Me_2C_6H_3$, Ar′ = Ar″ = Ph

c: Ar = 2-MeC_6H_2, Ar′ = Ar″ = Ph

d: Ar = Ar′ = Ar″ = Ph

e: Ar = Mes, Ar′ + Ar″ = 2,2′-$C_6H_4C_6H_4$

f: Ar = Ar′ = Ar″ = Mes

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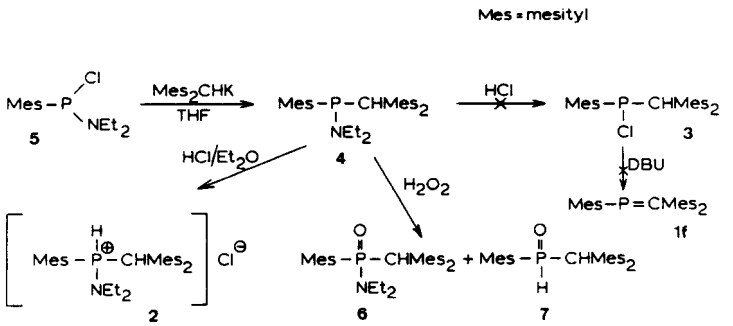
It was therefore of interest to investigate whether the increase of steric hindrance by introduction of *ortho*-methyl substituents into the C-aryl groups would further enhance the stability of the phosphaalkenes. For this reason, we attempted to synthesize trimesitylphosphaethene (**1f**). While this goal could not be achieved because steric crowding turned out to be excessive, for exactly the same reason we observed the formation of an intermediate **2** which, we feel, has an interesting bearing on the matter of acid catalyzed nucleophilic substitution at trivalent phosphorus, certain mechanistic aspects of which are still a topic of active discussion.

RESULTS AND DISCUSSION

Attempted Synthesis of Trimesitylphosphaethene (**1f**)

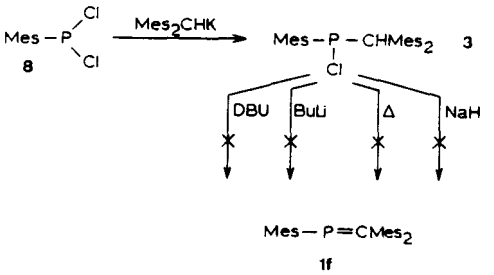
For the synthesis of **1f** by a well-established approach,[1] **3** was required as a precursor which we intended to obtain as indicated in Scheme 1. The intermediate **4** was prepared by reaction of **5** with α-potassiodimesitylmethane and characterized by its elemental analysis, ^{1}H and ^{31}P-NMR spectra, and by its conversion with H_2O_2 to **6**. In this latter reaction, besides **6** (dimesitylmethyl)mesitylphosphine oxide (**7**) was formed; formally, **7** is the product of hydrolysis of **4**, but its ready formation from the strongly hindered **4** is surprising. At room temperature, the ^{1}H-NMR spectrum of **4** was poorly resolved due to hindered rotation. Unfortunately, we could not determine the rotational barrier from temperature dependant NMR spectroscopy as the signals of the arylmethyl groups and of the aromatic protons were too complex. However, at 202 K, the N-ethyl groups showed two separate methyl triplets with coalescence at 320 K (250 MHz, $\delta = 0.49$ ppm, $\Delta\nu = 50$ Hz) from which a rotational barrier of $\Delta G^* = 15.8$ kcal · mol^{-1} can be derived. Even though the nature of the conformational movement involved has not been identified, it is evident that **4** is a rather crowded molecule.

Based on our previous experience,[1] we expected that treatment of **4** with dry gaseous hydrogen chloride in diethyl ether would easily furnish **3**. To our surprise we observed the formation of **2** instead. The structure of **2** follows from the elemental analysis and from the spectral data, in particular the ^{31}P-NMR spectrum. The ^{31}P



SCHEME 1

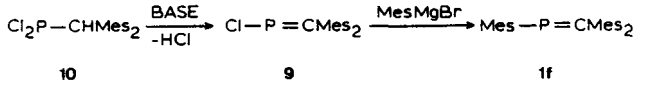
chemical shift (δ = 31.9 ppm) is in agreement with the proposed structure, and the $^1J(PH)$ = 540 Hz (doublet) unambiguously indicates the presence of one phosphorus hydrogen bond in a phosphonium salt. Again, the ^{1}H-NMR spectrum (250 MHz) was rather complex at room temperature. The decoalescence of the CH_3 triplet of the N-ethyl group at δ = 0.84 ppm occurred at 285 K (250 MHz; $\Delta\nu$ = 55.1 Hz) with a rotational barrier of ΔG^* = 13.9 kcal · mol^{-1}. The coalescence of the aromatic protons of the two C-mesityl groups occurred at 265 and 285 K, respectively (ΔG^* = 13.3 (δ = 6.91 ppm $\Delta\nu$ = 23.5 Hz) and 14.1 kcal · mol (δ = 6.75 ppm, $\Delta\nu$ = 42.5 Hz), respectively). The non-equivalence of the C-mesityl protons is probably due to diastereotopicity of the mesityl groups; it is not clear whether hindered rotation of the dimesitylmethyl group as a whole is also involved. The coalesence of the *ortho*-methyl signals of the P-mesityl group (δ = 6.92 and 7.12 ppm (220 K); recognizable by the phosphorus coupling at low temperature) was—by extrapolation—estimated to occur at ca. 340 K; it could not be observed directly because **2** decomposed at 330 K in chloroform to give unidentified products.



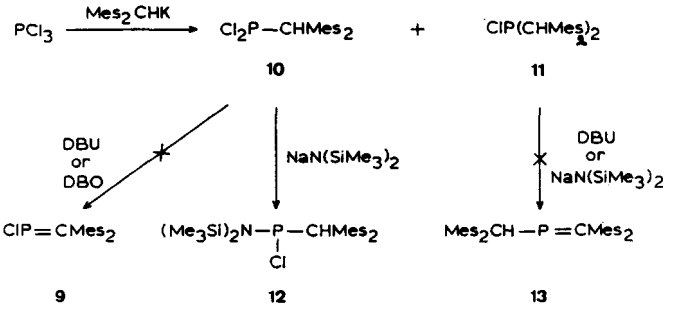
SCHEME 2

As the route of Scheme 1 did not lead to the desired **3**, we investigated a more direct route to **3** which was more successful. The reaction of α-potassiodimesitylmethane with dichloromesitylphosphine (**8**) gave **3** in ca. 95% yield (Scheme 2); **3** was characterized by its ^{1}H- and ^{31}P-NMR spectra and its field desorption mass spectrum. Subsequently, the elimination of hydrogen chloride from **3** was attempted. Reaction with DBU in boiling THF or toluene gave unchanged **3**, according to the ^{1}H-NMR spectrum. After prolonged heating with DBU in toluene (77 h), **3** decomposed to give dimesitylmethane, unidentified products and DBU.HCl (88%). In the ^{31}P-NMR spectrum, the typical low field signals of phosphaalkene phosphorus were not observed. With *n*-butyllithium, only one detectable phosphorus compound ($\delta(^{31}P)$ = −15.1 ppm) was formed in low yield. In an attempt to eliminate HCl by pyrolysis, **3** gave a mixture of twelve unidentified compounds (^{31}P-NMR) and evolution of gaseous acid, probably HCl. Finally, the elimination was attempted with a very small base, sodium hydride, in order to minimize steric obstruction of approach of the base to the carbon-attached hydrogen, the latter being a prerequisite for the intended elimination. However, according to ^{1}H-NMR spectroscopy, **3** did not react with NaH in THF.

In a third approach towards **1f**, we tried to make use of the recently synthesized P-chlorophosphaalkenes[4] (Scheme 3). If **9** could be prepared, its reaction with mesitylmagnesium bromide would be expected to lead to **1f** in analogy to a similar conversion of a P-chlorophosphaalkene to a P-alkylphosphaalkene.[5]



SCHEME 3



SCHEME 4

The synthesis of the required precursor **10** gave unexpected problems. Although it was obtained by the reaction of α-potassiodimesitylmethane with a tenfold excess of phosphorus trichloride (Scheme 4), ca. 40% of **11** were also formed as by-product. The observation that the carbanion reacts faster with the less electrophilic and more hindered species $RPCl_2$ than with phosphorus trichloride, cannot be explained at the moment. It is, however, in line with the following observations. Burg and Slota[6] found that two equivalents of methylmagnesium bromide reacted with phosphorus trichloride to give 62% trimethylphosphine. Reaction of arylmagnesium bromides with phosphorus trichloride also led to substantial amounts of disubstituted phosphines.[7] Klebach observed disubstitution when **8** was reacted with α-lithiodiphenylmethane;[1,8] similarly, we found on reaction of **8** or of *t*-$BuPCl_2$ with α-potassiodiphenylmethane 25% or 45% of $MesP(CHPh_2)_2$ or *t*-$BuP(CHPh_2)_2$, respectively. However, when α-potassiodimesitylmethane reacted with $MesPCl_2$, no disubstitution occurred (Scheme 2); apparently the second substitution reaction is prevented in this particular case by the bulkiness of the three mesityl groups already present in **3** (Scheme 1).

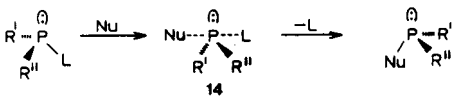
Compounds **10** and **11** could be separated by crystallization from hexane; the crystals of **10** and **11** differed in shape and colour. By separating them manually, followed by repeated crystallizations, **10** was obtained in a pure form. Elimination of hydrogen chloride from **10** with DBU in THF gave, besides DBU.HCl (^{1}H-NMR), a precipitate with a ^{31}P-NMR chemical shift of 91 ppm, which was not identified. With DBO (diazabicyclo[2.2.2]octane), successfully used in the preparation of other P-chlorophosphaalkenes,[4] eight unidentified phosphorus compounds (^{31}P-NMR) were formed. Reaction of sodium hexamethydisilyl amide with **10** gave a substitution product **12** according to the ^{31}P-NMR spectrum (δ = 166 ppm) and the ^{1}H-NMR spectrum ($\delta(SiC\underline{H}_3)$ = 0.22 ppm, $^4J(PH)$ = 1.8 Hz and $\delta(C\underline{H}Mes_2)$ = 5.53, $^2J(PH)$ = 8 Hz). An attempt to synthesize the strongly hindered **13** by elimination of hydrogen chloride from **11** with DBU gave unchanged starting material.

The failure of **3**, **10** and **11** to react with a base under elimination of HCl probably has a common cause. As the phenyl analogues of **3** and **10** eliminate HCl quite smoothly, we assume that the bulkiness of the mesityl groups is responsible. One might consider that in **3** and **11**, the mesityl groups prevent a trans coplanar conformation of the eliminating atoms H and Cl; however, a molecular model of **3** suggested that this conformation is not more unfavourable than others. A more likely possibility is that the base is prevented from reaching and attacking the hydrogen. This argument would not hold for sodium hydride, but it is doubtful whether hydride is a suitable base for hydrogen chloride elimination, as no example of a hydride-induced elimination yielding a phosphaalkene has been reported in the literature.[9]

Mechanistic implications of the formation of dimethylamino(dimesitylmethyl)-mesitylphosphonium chloride (2)

While the primary goal of our investigation, the synthesis of **1f**, was not achieved so far, the formation of **2** was of interest as a spin-off concerning substitution reactions of phosphorus(III) compounds. It was quite surprising that **4**, on reaction with hydrogen chloride underwent protonation instead of the usual substitution.[1] Furthermore, it should be emphasized that phosphorus and not nitrogen was protonated although the latter is normally considered to be more basic. However, the basicity order is not clear-cut. In general, phosphines are less basic than amines, but some trialkyl phosphines have pKa's larger than 9.[10] Electron withdrawing substituents lower the pKa, but it is difficult to estimate whether in aminophosphines, the lone pair of nitrogen raises the pKa by interaction with d-orbitals of phosphorus to such an extent that the effect to the electronegativity of nitrogen is overcompensated. It should be pointed out in this connection that the nucleophilic reactivity of aminophosphines resides at phosphorus, as exemplified by the reaction with methyl iodide.[6] Unfortunately, the pKa's of aminophosphines have not been measured as aminophosphines hydrolyze in water.[11]

Nucleophilic substitution reactions at P(III) compounds have been shown in most cases to proceed by a genuine S_N2(P(III)) type mechanism involving inversion at phosphorus via the transition state **14** (Scheme 5).[12] However, in transamination reactions, the situation is more complicated. In this case, inversion is also observed[13,14] and the more basic amine (which is considered to be the best nucleophile) replaces the less basic amine; but the reaction is strongly influenced and catalyzed by acid,[15,16] e.g. by ammonium chloride impurities, present in aminophosphines. When ammonium chloride impurities were rigorously removed, aniline (which is the less basic amine) did not replace a dialkylamine, but in the presence of traces of ammonium salts the reaction proceeded for 10–70% depending on the acid concentration. These observations prompted Batyeva *et al.*[16] to postulate that the nitrogen, which was assumed to be more basic than phosphorous, is protonated to yield **15**, whereupon phosphorus becomes more electrophilic and thus more susceptible to nucleophilic substitution (Scheme 6). A similar course of events was postulated in other exchange reactions of aminophosphines.[17] On the other hand, Dahl[14] has presented evidence that protonation on phosphorus is more likely. One indication was that phenylamino phosphines reacted faster than dialkylphosphines under acidic conditions, although the phenylamino nitrogen is less basic than the dialkylamino



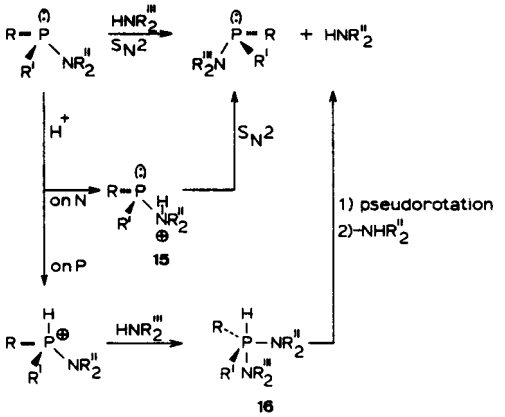
SCHEME 5

nitrogen. A second indication for P-protonation and involvement of a phosphorane structure **16** (Scheme 6) as an intermediate (and not as a transition state!) in the substitution reaction was a transamination reaction of a cyclic five-membered ring phosphine. In such a reaction, the S_N2 transition state **14** (Scheme 5) with R′ and R″ forming a five-membered ring, would be very unfavourable because of the well-known strain connected with a five-membered ring in a diequatorial position of the triagonal bipyramide; nevertheless, the reaction proceeded quite smoothly. There are other reports in the literature postulating the intermediacy of TBP phosphoranes in reactions of aminophosphines, e.g. in the reaction with carbonyl electrophiles;[18] a convincing example of P-protonation followed by TBP-formation is found in $[HP(OCH_2)_3N]^{\oplus}$.[19]

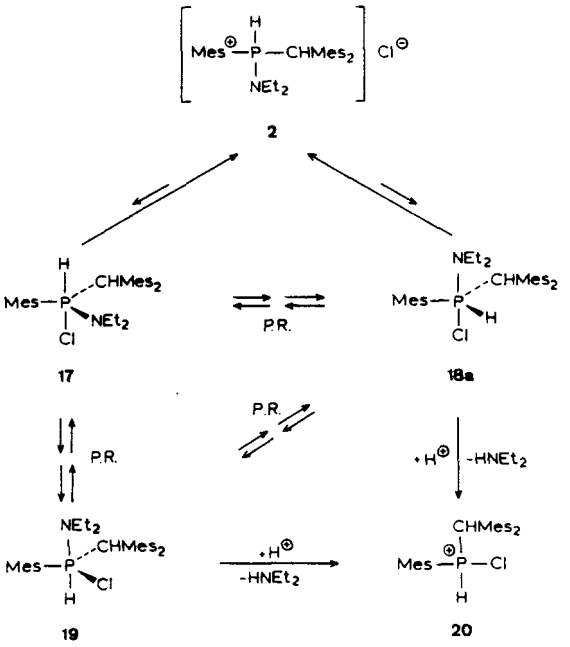
The importance of the formation of **2** in the discussion described here resides in the fact that it forms a "solidified" proof of the hitherto postulated first step, i.e. of P-protonation. To our knowledge, **2** is the first example of a stable aminophosphonium salt[11,20] with a hydrogen bound to phosphorus.

A question which remains is why **2** does not complete the reaction pathway to substitution. The answer is rather complex and cannot be given unequivocally. One trivial possibility would be that **2** is removed from an equilibrium and protected from further reaction in the solid state because it crystallizes from the reaction mixture. This possibility was readily excluded by showing that **2** is stable in chloroform solution at ambient temperatures, even when hydrogen chloride is bubbled through the solution.

There are at least two other, more plausible explanations. The first one is that the chloride ion of **2** cannot add to phosphorus for steric reasons. On the basis of the



SCHEME 6



SCHEME 7

generally accepted rule that an incoming nucleophile occupies an apical position in the trigonal bipyramide (TBP) of the resulting phosphorane, two types of TBP's can be distinguished, i.e. one with hydrogen in an apical position (**17**; Scheme 7) and those with hydrogen in an equatorial position (**18**). Of **18**, there are three structural isomers which carry the diethylamino group (**18a**), the mesityl group (**18b**) and the dimesitylmethyl group (**18c**), respectively, in the second apical position. Only **18a** is shown in Scheme 7 as it may be assumed to be the most stable one because of the apicophilicty order [21,22] N > C which in the present case is further enhanced by the great bulkiness of the two carbon substituents. For the same reason, **17** is far more stable than **18**, because it has hydrogen in the preferred apical position; the other three groups should prefer the equatorial positions, both for electronic and in particular for steric reasons, as the situation is already rather congested in **2** (vide supra) and will become even more so in any phosphorane formed from it. However, the transformation of **2** to **17** happens to be the least favourable process for kinetic reasons as the chloride must approach the tetrahedron of the phosphonium ion at the most hindered face. According to models, this face is completely blocked by the three large substituents. The alternative mode of attack by chloride at a less hindered face would lead to one of the three isomers of **18** and is unfavourable for thermodynamic reasons. Both pathways being unfavourable, the normal addition of chloride may not proceed, and thus the reaction is irreversibly stopped at the level of **2**.

The second plausible possibility is the following. Although the equilibrium between **2** and a phosphorane will be shifted towards **2** even more strongly than usual because of steric factors, the formation of a phosphorane may still proceed to a small extent, but it is the further course of the reaction which is seriously impeded

by steric congestion. The next reaction step would have to be protonation at nitrogen followed by extrusion of diethylamine to furnish **20**. For this cleavage to occur, the P—N bond must occupy an apical position. This is not the case in the most favourable TBP **17** (nor in **18b** and **18c**); of the four structural isomers of the phosphorane which do fulfill this condition, **18a** and **19** are the least unfavourable ones because they have at least one relatively apicophilic group (Cl or H, respectively) in the second apical position. However, either they are still thermodynamically too unfavourable, or they are kinetically inaccessible because of high barriers for the required pseudorotations (Scheme 7, PR). Thus, as the diethylamino group cannot attain an apical position, the reaction goes back to **2**. In normal substitutions of this type, the intermediates are much less crowded and accordingly, the steric factors are sufficiently diminished to allow either attack by chlorine or pseudorotation to a TBP which permits extrusion of the diethylamino group. This is apparently the case even when the dimesitylmethyl group in **4** is replaced by the rather bulky diphenylmethyl group.[1]

An unequivocal rationalization of the lack of reactivity of **2** in the presence of hydrogen chloride cannot be given, but its formation as such shows that protonation on phosphorus is a possible and apparently a favourable reaction. It thus provides direct experimental evidence for the feasibility of the first step in the acid catalyzed nucleophilic substitution reaction. Although our results give only indirect information on the following step for the very reason that it does not occur in this case, the mechanistic sequence via phosphoranes (Scheme 6 and 7) is a logical follow-up and is well supported by other evidence.[14]

EXPERIMENTAL

General. 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 85% aqueous H_3PO_4 (external for ^{31}P) or tetramethylsilane (internal for ^1H). Unless otherwise stated, ^{31}P spectra are broad band decoupled. Reactions were performed under an argon or nitrogen atmosphere; small runs were performed in sealed, evacuated systems. Solvents were distilled from lithium aluminum hydride (alkanes, tetrahydrofuran, diethyl ether), magnesium alkoholate (ethanol, methanol), phosphorus pentoxide (chloroform, dichloromethane, carbon disulfide), potassium carbonate (acetone) or dried by azeotropic distillation (benzene, toluene). Melting points are uncorrected. Elemental analyses were performed by Organisch Chemisch Instituut TNO, Zeist.

Diethylamino(dimesitylmethyl)mesitylphosphonium chloride (**2**). Compound **4** (350 mg, 0.74 mmol) was dissolved in diethyl ether (40 mL). Hydrogen chloride was bubbled through the solution until colourless oil precipitated no longer. After 2h, this oil had crystallized to give colourless crystals of **2**, (319 mg, 91%), m.p. 139°C (dec). ^{1}H-NMR ($CDCl_3$, 48°C) δ = 0.84 (t, ^3J(HH) = 7 Hz, 6 H, $CH_2C\underline{H}_3$), 2.15 (s, 9 H, aryl Me), 2.21 (d, ^4J(PH) = 2 Hz, 3 H, aryl Me), 2.49 (bs, 6 H, aryl Me), 2.56 (bs, 6 H, aryl Me), 2.71–3.20 (m, 4 H, $C\underline{H}_2CH_3$), 5.78 (dd, ^2J(PH) = 32 Hz, ^3J(HH) = 10 Hz, methine H), 6.68 (s, 2 H, aryl H), 6.93 (bs, 3 H, aryl H), 6.97 (s, 1 H, aryl H), 8.98 ppm (dd, ^1J(PH) = 540 Hz, ^3J(HH) = 10 Hz, 1 H, P—H). ^{31}P-NMR ($CDCl_3$) δ = 31.9 pp. Mass spectrum (FD) m/z 473 $[M-HCl]^+$. Found: C, 75.06; H, 8.86; Cl. 7.09; N, 2.65; P, 6.17. $C_{32}H_{45}ClNP$ (M = 510.11) requires: C, 75.34; H, 8.89; Cl, 6.95; N, 2.75; P. 6.07.

Chloro(dimesitylmethyl)mesitylphosphine (**3**). A solution of α-potassiodimesitylmethane (11.0 mmol) in THF (50 mL) was added dropwise to a solution of **8**[23] (2.27 g, 10.2 mmol) in THF (25 mL) at −50°C. After slowly warming to room temperature, the solution was filtered and the filtrate evaporated (the filtration is cumbersome and leads to considerable loss of material, so that the yield of **3** obtained in this preparation is not typical and optimal; in later syntheses of other, comparable compounds, the reaction mixture was centrifuged under nitrogen instead, which leads to superior results). The solid residue (2.31 g)

consisted of a mixture of **3** (40% yield) and dimesitylmethane in a ratio of 3 : 1, according to the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$; only the signals of **3** are reported) δ = 2.13–2.57 (m, 27 H, CH_3), 6.08 (d, ^2J(PH) = 3.8 Hz, methine H), 6.62–6.85 ppm (m, 6 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 90.3 ppm. Mass spectrum m/z 436 $[M]^{+\cdot}$ (for $C_{28}H_{34}{}^{35}ClP$).

Diethylamino(dimesitylmethyl)mesitylphosphine (**4**). To a solution of **5**[1] (2.0 g, 7.8 mmol) in THF (25 mL) α-potassiodimesitylmethane (8.5 mmol) in THF (50 mL) was added dropwise at −50°C. After warming to room temperature, the precipitate was filtered off; the solvent was evaporated. The remaining yellow oil (2.6 g) was crystallized three times from pentane yielding colourless crystals of **4**, 1.8 g (49%), m.p. 145–150°C. ^{1}H-NMR ($CDCl_3$, 52°C) δ = 0.49 (t, ^3J(HH) = 7 Hz, 6 H, $CH_2C\underline{H}_3$), 2.11–2.77 (m, 27 H, aryl Me), 2.78 (quint, ^3J(HH) = ^3J(PH) = 7 Hz, 4 H, $C\underline{H}_2CH_3$) 5.67 (d, ^2J(PH) = 3.5 Hz, 1 H, methine H), 6.53 (s, 2 H, aryl H), 6.71 ppm (m, 4 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 52.9 ppm. Mass spectrum (FD) m/z 473 $[M]^{+\cdot}$. Found: C, 81.03; H, 9.22; N, 2.90; P, 6.62. $C_{32}H_{44}NP$(M = 473.65) requires: C, 81.14; H, 9.36; N, 2.96; P, 6.54.

Diethylamino(dimesitylmethyl)mesitylphosphine oxide (**6**). Compound **4** (4.5 g of a mixture of **4** and dimesitylmethane, ca. 1 : 1) was dissolved in acetone (50 mL) and H_2O_2 (4 mL, 35% in H_2O, 41 mmol) was added. The solution was heated under reflux for 1 h and then partially evaporated. The mixture was extracted with chloroform/water, the organic layer was dried with sodium sulfate and evaporated. Column chromatography (silicagel) of the residue with cyclohexane gave 1.58 g of a mixture of **6** and dimesitylmethane (ca. 1 : 1, ^{1}H-NMR). Elution with chloroform gave a second fraction of 1.56 g which consisted of 50% **6** and (dimesitylmethyl)mesitylphosphine oxide (**7**) (ca 1 : 1, ^{1}H-NMR). Crystallization of the chloroform fraction from diethyl either gave colourless crystals of **6**, 151 mg, m.p. 203–205°C. ^{1}H-NMR ($CDCl_3$) δ = 0.86 (t, ^3J(HH) = 6 Hz, 6 H $CH_2C\underline{H}_3$), 1.90–2.22 (m, 27 H, aryl Me), 2.44–2.89 (m, 4 H, $C\underline{H}_2CH_3$), 5.18 (d, ^2J(PH) = 22 Hz, 1 H, methine H), 6.63 (s, 2 H, aryl H), 6.78 ppm (bs, 4 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 41.1 ppm. Mass spectrum (FD) m/z 489 $[M]^{+\cdot}$. Found: C, 78.73; H, 9.19; N, 2.75; P, 6.11. $C_{32}H_{44}NOP$ (M = 489) requires: C, 78.49; H, 9.06; N, 2.86; P, 6.32. **7**: ^{1}H-NMR ($CDCl_3$) δ = 2.04–2.35 (m, 27H, aryl Me) 4.46 (d, ^2J(PH) = 20 Hz, 1 H, methine H) 6.76 ppm (bs, 6 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 19.2 ppm. Mass spectrum (FD) m/z 418 $[M]^{+\cdot}$.

Dichloro(dimesitylmethyl)phosphine (**10**) *and chlorobis(dimesitylmethyl)phosphine* (**11**). A solution of α-potassiodimesitylmethane (19.1 g, 67.6 mmol) in THF (500 mL) was added dropwise to phosphorus trichloride (50 mL, 600 mmol) in THF (50 mL) at −65°C under vigorous stirring. After slowly warming to room temperature, the solution was evaporated and the residue was extracted with hexane (200 mL). After filtration and evaporation of the hexane an orange oil (15.8 g) remained which solidified slowly. Crystallization from hexane gave a mixture of **10** and **11** (10 g). After a second crystallization from hexane, both compounds crystallized: **10** gave yellowish, irregular but compact crystals, while **11** gave colourless, regular cubes. The crystals were separated manually and **10** was recrystallized twice (2.07 g, 7%), m.p. 112–126°C. ^{1}H-NMR ($CDCl_3$) δ = 2.24 (s, 6 H, p-Me), 2.44 (d, ^4J(PH) = 1.5 Hz, 12 H, o-Me), 5.62 (d, ^2J(PH) = 9 Hz, 1 H, methine H), 6.70 ppm (s, 4 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 188 ppm. Mass spectrum m/z (%) 317 (1.2) $[M{-}Cl]^+$, 252 (22) $[Mes_2CH_2]^{+\cdot}$, 251 (100) $[Mes_2CH]^+$, 221 (17) $[C_{17}H_{18}]^{+\cdot}$. Exact mass m/z 317.1209 ($C_{19}H_{23}ClP^{+\cdot}$ requires 317.1226). **11**: M.p. 163°C (dec.). ^{1}H-NMR ($CDCl_3$) δ = 1.89–2.84 (m, 36 H, aryl Me), 5.27 (d, ^2J(PH) = 4 Hz, 2 H, methine H), 6.78 ppm (s, 8 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 126 ppm.

Attempted elimination of hydrogen chloride from **3**

A. With diazabicycloundecene (DBU). Compound **3** (581 mg, 1.33 mmol) was dissolved in THF (25 mL) and DBU (205 μL, 1.33 mmol) in THF (10 mL) was added dropwise. According to a ^{1}H-NMR spectrum of the solution, recorded after stirring for 15 min, **3** was unchanged. Excess DBU was added (200 μL, 1.31 mmol), and the solution was heated under reflux for 30 min. **3** Remained unchanged (^{1}H-NMR). After refluxing for 77 h, **3** was decomposed; according to ^{1}H-NMR spectroscopy, dimesitylmethane and a precipitate of DBU.HCl (220 mg, 88%) had been formed.

B. With butyllithium. Compound **3** (244 mg, 0.56 mmol) was dissolved in THF (20 mL) and n-BuLi (0.5 mL of a 1.17 N solution in hexane, 0.58 mmol) in THF (3 mL) was added dropwise at −65°C. According to a ^{1}H-NMR spectrum, **3** had not reacted after warming to room temperature. After cooling to −65°C again, excess n-BuLi (0.5 mL, 0.58 mmol) in THF (3 mL) was added. The solution became orange; after warming to room temperature, it turned brown. According to a ^{1}H-NMR spectrum of the solution, **3** had disappeared, and the solution contained only one phosphorus compound of very low concentration (δ^{31}P = −15.1 ppm, possibly n-butyl(dimesitylmethyl)mesitylphosphine).

C. By pyrolysis. Compound **3** (97 mg, 0.22 mmol) was heated in a round-bottom flask to 200°C for 30 min under an argon atmosphere. A test with pH paper indicated the evolution of acid. Dimesitylmethane had sublimed to the wall of the flask above the oil level (^{1}H-NMR). A ^{31}P-NMR spectrum of

the reaction mixture revealed that **3** had disappeared; there were 12 phosphorus compounds present. No low field signal could be observed.

D. With NaH. To NaH (70 mg of a suspension in paraffin, washed three times with diethyl ether (4 mL); 1.6 mmol) a solution of **3** (164 mg, 0.38 mmol) in THF (ca. 10 mL) was added. After stirring 1 h at room temperature and after heating under reflux for 1 h, **3** had not reacted (^{1}H-NMR).

Attempted elimination of hydrogen chloride from **10**

A. With DBU. To a solution of **10** (160 mg, 0.5 mmol, contaminated with 15% **11**) in THF (5 mL), DBU (120 μL, 0.79 mmol) was added dropwise, whereupon a precipitate was formed. This precipitate (δ^{31}P ($CDCl_3$) = 91.5 ppm, (possibly ($Mes_2CHPClDBU^+$)Cl^-) was filtered off and washed twice with cyclohexane (ca. 3 mL), m.p. 175–195°C. After contact with air the $\delta(^{31}P)$ was 40.2 ppm; according to a ^{1}H-NMR spectrum this unidentified compound contained a P—H bond (δ = 7.39, ^1J(PH) = 488 Hz).

B. With sodium hexamethyldisilylamide. To a solution of **10** (160 mg, 0.45 mmol) in THF (10 mL), sodium hexamethyldisilylamide (130 mg, 0.71 mmol) was added at room temperature. The solution turned brown on addition and a precipitate (m.p. > 300°C) was formed. The solution contained 92% **12** and 8% **11** (introduced with the starting material, ^{31}P-NMR). ^{1}H-NMR ($CDCl_3$) δ = 0.22 (d, ^4J(PH) = 1.8 Hz, SiMe, 18 H), 2.18 (s, 6 H, p-Me), 2.44 (s, 12 H, o-Me), 5.53 (d, ^2J(PH) = 8 Hz, 1 H, methine H), 6.76 ppm (s, 4 H, aryl H). ^{31}P-NMR ($CDCl_3$) δ = 166 ppm. Mass spectrum m/z (%) 423 (18), 421 (35) [M^+—$SiMe_3$—H + O] (oxygen probably introduced while sampling in contact with air), 252 (37) [$Mes_2CH_2]^+$, 251 (100) [$Mes_2CH]^+$.

C. With diazabicyclooctane (DBO). Compound **10** (80 mg, 0.23 mmol) was dissolved in THF (5 mL) and DBO (140 mg, 1.25 mmol) was added whereupon a white precipitate formed. According to a ^{31}P-NMR spectrum, there were 8 phosphorus compounds ($\delta(^{31}P)$ = 132–133 ppm) present.

Attempted elimination of hydrogen chloride from **11**. In two separate experiments, **11** was mixed in THF with DBU and sodium hexamethyldisilylamide, respectively, on a 0.2 mmol scale. After heating to reflux for 6 h and 40 min, respectively, ^{1}H-NMR spectra of samples showed unchanged **11** only.

REFERENCES AND NOTES

1. Th. A. van der Knaap, Th. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam and M. Konijn, *Tetrahedron*, **40**, 765 (1984).
2. G. Becker, W. Uhl and H. J. Wessely, *Z. Anorg. Allg. Chem.*, **479**, 41 (1981).
3. Th. A. van der Knaap and F. Bickelhaupt, *Chem. Ber.*, **117**, 915 (1984).
4. R. Appel and A. Westerhaus, *Angew. Chem.*, **92**, 578 (1980).
5. R. Appel and U. Kündgen, *Angew, Chem.*, **94**, 227 (1982).
6. A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).
7. M. Yoshifuji, personal communication.
8. Th. C. Klebach, personal communication.
9. R. Appel, F. Knoll and I. Ruppert, *Angew. Chem.*, **93**, 771 (1981).
10. L. Maier in *Organic Phosphorus Compounds* (G. M. Kosolapoff and L. Maier, ed.; Wiley-Interscience, New York, 1972), Vol. 1, p. 77.
11. L. A. Hamilton and P. S. Landis in *Organic Phosphorus Compounds* (G. M. Kosolapoff and L. Maier, ed.; Wiley-Interscience, New York, 1972), Vol. 4, p. 504.
12. For a leading reference see M. Mikolajczyk, *Pure Appl. Chem.*, **52**, 959 (1980).
13. L. Lafaille, F. Mathis and R. Burgada, *C. R. Acad. Sci., Ser. C*, **270**, 1138 (1970).
14. O. Dahl, *Tetrahedron Lett.*, **22**, 3281 (1981); J. Nielsen and O. Dahl, *Phosphorus and Sulfur*, **18**, 443 (1983).
15. J. A. Mosbo, *Phosphorus and Sulfur*, **4**, 273 (1978).
16. E. S. Batyeva, V. A. Al'fonsov, G. U. Zamaletdinova and A. N. Pudovik, *J. Gen. Chem. USSR*, **46**, 2204 (1976).
17. L. Horner and M. Jordan, *Phosphorus and Sulfur*, **8**, 235 (1980).
18. J. H. Hargis and G. A. Mattson, *J. Org. Chem.*, **46**, 1597 (1981).
19. J. C. Clardy, D. S. Milbrath, J. P. Springer and J. G. Verkade, *J. Am. Chem. Soc.*, **98**, 623 (1976).
20. P. Beck in *Organic Phosphorus Compounds* (G. M. Kosolapoff and L. Maier, ed.; Wiley-Interscience, New York, 1972), Vol. 2, p. 189.
21. S. Trippett, *Phosphorus and Sulfur*, **1**, 89 (1976).
22. J. Emsley and D. Hall, *The Chemistry of Phosphorus* (Harper and Row, London, 1976), p. 65.
23. W. C. Davies, *J. Chem. Soc.*, 462 (1935).