1-(2,4,6-Tri-*tert*-butylphenyl)-3-methylphosphole: A Phosphole with a Significantly Flattened Phosphorus Pyramid Having Pronounced Characteristics of Aromaticity

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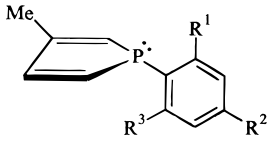
Abstract: Single-crystal X-ray analysis of 1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphosphole, synthesized to test the effect of the strongly sterically demanding P-substituent on the geometry of the molecule, revealed that the phosphorus pyramid was drastically flattened; the normal out of plane angle of 65° (formed between the P-substituent and the ring C_2-P-C_5 plane) was reduced to 45.9°. Consistent with strong electron delocalization, the C_3-C_4 bond length was dramatically shortened relative to that for other phospholes, and the Bird index of aromaticity was 56.5, almost the equivalent of that in pyrrole (59). The phosphole ring, normally resisitant to electrophilic substitutions, underwent reaction with acetyl chloride−aluminum chloride, consistent with considerable cyclic electron delocalization.

Introduction

The family of phospholes constitutes an important place in contemporary phosphorus chemistry, and detailed reviews of this area[1] and of aromaticity in general[2] have recently been published. As members of the group of heterocyclopentadienes, phospholes might be expected to exhibit the cyclic electron delocalization so characteristic of this structural type. In fact, for the phospholes reported thus far, there is little delocalization, and this is attributed to the pyramidal shape retained at phosphorus that interferes with efficient orbital interaction.[1a] However, theoretical calculations[3] have suggested that if the phosphorus atom could adopt planar geometry, then strong delocalization, on the order of that of thiophene,[1c] could prevail. We have embarked on an experimental program to test this idea. Our premise is that placement of very large, space-demanding substituents on phosphorus might induce a degree of flattening of the phosphorus pyramid that would permit significant electron delocalization which would be reflected in the physical and chemical properties of the system. A recent report[4] indeed makes a connection between pyramidal character at P and the degree of delocalization, but in the opposite sense: placing two acetylenic substituents at the α-positions caused an increase in pyramidal character relative to 1-benzylphosphole[5] as seen in an X-ray analysis, as well as lengthening of the C_3-C_4 and P−C bonds. Another approach to planarization of phosphorus has been taken by Schmidpeter that involves placement of electron-withdrawing triphenylphosphonio substituents at the two positions adjacent to phosphorus; this was effective in the isophosphindole system[6a] and the 1,2-diphosphole system.[6b]

The first compound (**1**) prepared in this study contained the 2,4-di-*tert*-butyl-6-methylphenyl substituent,[7] and it was readily apparent from the photoelectron spectrum that increased electron delocalization due to the partially planarized structure was present; the ionization energy of the lone pair of **1** was the lowest ever recorded for a phosphole and differed substantially from that of the tetrahydro derivative.[8] We use the angle of deflection



	R^1	R^2	R^3
1	t-Bu	t-Bu	Me
2	i-Pr	i-Pr	i-Pr
3	t-Bu	t-Bu	t-Bu

of the P-substituent from the plane of C_2-P-C_5 in the phosphole ring as a convenient descriptor of the flattening; in an uncrowded phosphole such as 1-benzyl,[5] this angle was determined by X-ray diffraction analysis to be 66.9°. In phosphole **1**, calculations give an angle of 57.4° to account for the lone pair ionization energy.[8] The second phosphole (**2**) prepared had the 2,4,6-triisopropylphenyl substituent, and X-ray diffraction analysis suggested that partial flattening of the phosphorus pyramid had occurred with an out of plane angle of 58°.[9]

We have now succeeded in preparing phosphole **3** which has the well-known highly space-demanding 2,4,6-tri-*tert*-butylphe-

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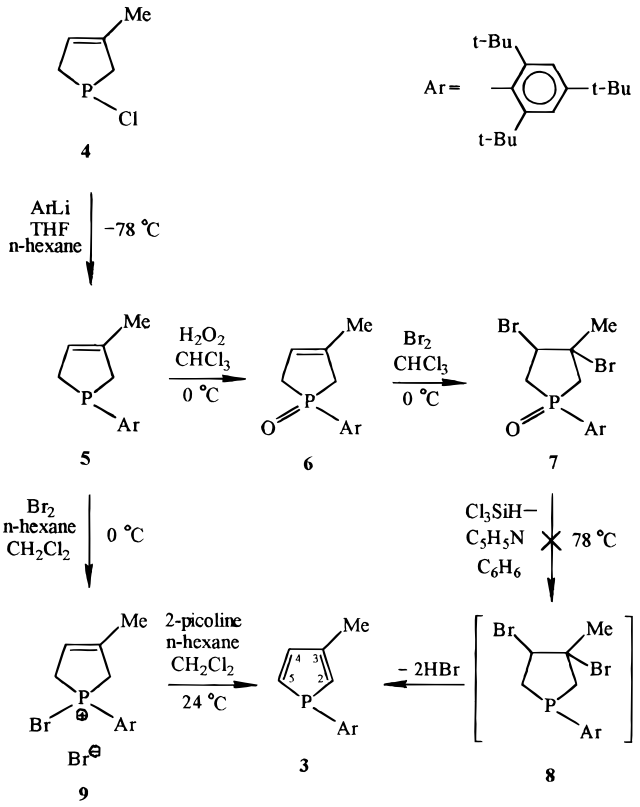
Scheme 1



nyl substituent. The synthesis and some properties are described in this paper. It will be seen from both its physical and chemical properties that the compound does indeed seem to have a quite significant degree of electron delocalization, adequate to give it a place in the family of "aromatic" heterocyclopentadienes.

We note that a phosphindole has been reported with the same large P-substituent, but with no assessment of degree of pyramidal character or delocalization.[10]

Results and Discussion

Synthesis and NMR Characterization of Phosphole 3. The reactions used in our attempts to synthesize phosphole **3** are summarized in Scheme 1. The starting material was 1-chloro-3-phospholene (**4**). Steric factors prevented the formation of the aryl Grignard reagent from the bromotri-*tert*-butylbenzene; hence, we could not use our earlier method for the syntheses of crowded phospholenes.[7,9] The synthesis could, however, be accomplished by reaction of the aryllithium reagent with the chlorophospholene (**4**). The pathway followed earlier to phospholes **1** and **2** involved the sequence shown as **4** → **5** → **6** → **7** → **8**, in which the appropriate dibromophospholane **8** is the immediate precursor of the phosphole on dehydrobromination. The sequence as used in the present case was successful only through the synthesis of the dibromophospholane oxide **7**, since, due to side reactions, this compound was very difficult to reduce to the necessary phospholane stage (**8**). A second sequence, developed early in our studies on phospholes[11] proved to be more successful. The 3-phospholene **5** was converted to the bromophospholenium bromide **9** by the addition of 1 equiv of bromine; **9** was then subjected to the Mathey procedure[12] of dehydrobromination with 2-picoline to form the desired phosphole **3** in a satisfactory yield of 62%.

Table 1. ^{13}C NMR Data for Phosphole **3** (and the Phenyl Analogue[13]) in $CDCl_3$[a]

	δ	J_{PC} [Hz]
C_2	125.8 (128.5)	11.1 (1.2)
C_3	138.5 (147.4)	23.4 (8.8)
C_4	131.0 (140.1)	20.5 (7.6)
C_5	132.0 (136.0)	7.7 (5.3)
$C_3\underline{C}H_3$	19.0	3.8
C_7	121.8	18.2
C_8	151.9	2.2
C_9	119.6	
C_{10}	150.0	
C_{11}	122.9	9.1
C_{12}	158.6	12.3

[a] Other data: 35.1 ($C_8\underline{C}Me_3$), 35.2 ($C_{10}\underline{C}Me_3$), 39.0 (J = 2.4, $C_{12}\underline{C}Me_3$), 31.4 ($C_8C(\underline{C}H_3)_3$), 31.8 ($C_{10}C(\underline{C}H_3)_3$), 33.4 ($J$ = 4.1, $C_{12}\overline{C}(\underline{C}H_3)$).

Phosphole **3** could be purified by column chromatography and crystallization and was characterized by mass and NMR spectroscopic methods. The ^{31}P NMR signal for the phosphole appeared at δ −0.4, a value differing little from that (δ 1.8) of the related phosphole **1**.[7] Calculations suggest that flattening of the phosphorus pyramid and increased delocalization can be expected to have a relatively small effect on the phosphorus shift.[3]

In the ^{13}C NMR spectrum of phosphole **3** (Table 1), the effects on the phosphole ring carbons from the planarization and increased electron delocalization can be clearly seen. These effects are especially strong at the β-carbons, as is apparent when a comparison is made with the spectrum of the uncrowded 1-phenyl analogue (Table 1).[13] Thus, in **3**, both β-carbons are upfield-shifted by about 9 ppm. Nonbonded steric interactions with the aryl substituent should be minimal at the β-carbons and cannot account for this upfield shifting. Computations of the carbon spectra for 1*H*-phosphole in both planar and pyramidal form support this conclusion.[14] At the α-carbons of **3**, upfield shifting was also observed but was of smaller magnitude (at C_2, 2.7 ppm; at C_5, 4.0 ppm). Also striking was the substantial increase in phosphorus coupling to the ring carbons of **3** compared to that in the 1-phenyl analogue[13] (Table 1). It is possible that the coupling effect is related to electron delocalization and the increased electron density at the ring carbons, but it is also possible to develop an explanation based upon relations established from many studies of other phosphorus compounds.[15] Thus, two-bond P−C coupling is empirically related to the orientation of the phosphorus lone pair to the coupled carbon. As the lone pair moves closer to a carbon, the coupling constant increases. This is the case when a phosphole is planarized. One-bond P−C coupling is sensitive to the hybridization at phosphorus, increasing as the degree of s-character increases. Increased planarization at phosphorus would be accompanied by a change in this direction, as sp^2 hybridization is approached in the fully planar form. The carbon shifts and coupling constants for the phosphole ring carbons of **1**[7] and **2**,[9] where the crowding is less than that in **3**, show in general the same trends but of intermediate magnitudes.

The ^{13}C NMR signals for the aryl substituent of **3** clearly show that the benzene and phosphole rings are orthogonal to each other in the conformation adopted at room temperature,

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for **3**

P_1-C_5	1.741(8)	C_9-C_{10}	1.379(10)
P_1-C_2	1.746(9)	$C_{10}-C_{11}$	1.389(10)
P_1-C_7	1.812(8)	$C_{11}-C_{12}$	1.395(10)
C_2-C_3	1.347(12)	$C_5-P_1-C_2$	91.7(5)
C_3-C_4	1.402(12)	$C_5-P_1-C_7$	118.3(4)
C_3-C_6	1.524(12)	$C_2-P_1-C_7$	121.7(4)
C_4-C_5	1.352(12)	$C_3-C_2-P_1$	109.9(7)
C_7-C_{12}	1.417(9)	$C_2-C_3-C_4$	112.9(8)
C_7-C_8	1.449(9)	$C_5-C_4-C_3$	115.2(8)
C_8-C_9	1.383(9)	$C_4-C_5-P_1$	108.4(7)

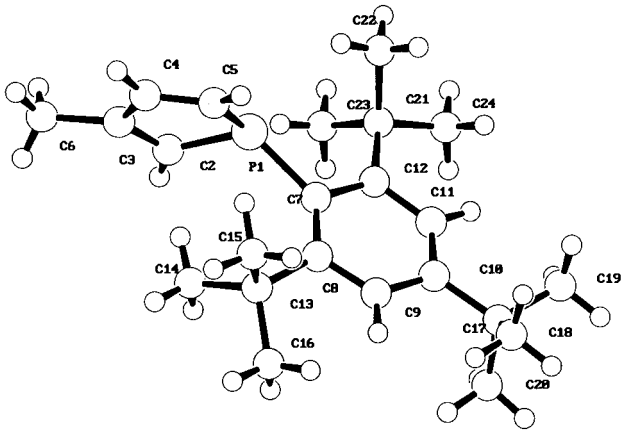

Figure 1. Perspective view of phosphole **3**.

just as expected from studies on phosphole **1** which showed the same effect.[7] Thus, there are separate signals for the two *ortho* carbons, as well as for the *meta* carbons, and also for the *tert*-butyl groups attached to the *ortho* carbons. As a result of the fixed conformation, one edge of the benzene ring is held in closer proximity to the phosphorus lone pair orbital than is the other as expressed in structure **3**, and there are noticeable differences in the coupling constants to carbons on the different edges of the benzene ring (Table 1).

The proton NMR spectrum of phosphole **3** resembled that of phospholes **1** and **2** and had no remarkable features that could arise from the increased electron delocalization. We observed, however, a surprisingly large four-bond P-coupling to the 3-methyl group; the value was 7.3 Hz, but was only 1.5 Hz in phosphole **1**.

Molecular Parameters for Phosphole 3 from X-ray Diffraction Analysis. Molecular parameters of phosphole **3** are supplied in Table 2. The conclusion drawn from the ^{13}C NMR spectrum that the phosphole and benzene rings were orthogonal to each other was confirmed (see Figure 1). Another significant observation on **3** was the very pronounced flattening of the phosphorus pyramid. To describe this effect, we use the angle (designated α) of deflection of the carbon of the P-substituent from the plane of C_2-P-C_5 of the phosphole ring (the degree of planarization could also be expressed by the π-orbital axis vector method,[16] as was done for phosphole **1**). For the unhindered 1-benzylphosphole,[5] α is 66.9°. Replacement of benzyl by 2,4,6-triisopropylphenyl[9] caused measurable flattening of the phosphorus pyramid (α 58.0°). In the more crowded phosphole **3**, α is reduced even further, as predicted, to a value of 45.0°, and the molecule is of great significance in the continuing study of the influence of planarization at phosphorus on electron delocalization. The general shape of the phosphole ring was not distorted by the steric crowding and resembled that of 1-benzylphosphole.[5] This phosphole had a C_2-P-C_5 angle of 90.7° with P out of the plane of $C_2-C_3-C_4-C_5$ by 0.21 Å; for phosphole **3**, these values were 91.7° and 0.294 Å.

Table 3. Selected Bond Lengths [Å] and the Bird Index of Aromaticity for Benzylphosphole (BP), Phospholes **2** and **3**, and the Phospholide Ion (PI)

	BP[5]	**2**[9]	PI[17]	**3**
$P-C_2$, $P-C_5$	1.786[a]	1.780[a]	1.751[a]	1.743[a]
C_3-C_4	1.438	1.436	1.424	1.402
C_2-C_3, C_4-C_5	1.343[a]	1.353[a]	1.396[a]	1.350[a]
BI	35.5	40.4		56.5

[a] Average values.

Of critical importance in the assessment of the extent of electron delocalization in a cyclic compound is the determination of bond lengths. In 5-membered heterocycles, electron release from the heteroatom is well-known to cause shortening of the bond to the sp^2 α-carbon. Table 3 shows the average P−C bond lengths measured for the series of 1-benzylphosphole,[5] phospholes **2**[9] and **3**, and the phospholide ion.[17] As can be seen there is a relatively great reduction in the average P−C bond length in **3**, consistent with considerable electron delocalization. Another indication of the extent of P−C bond shortening is provided by comparison of the average internal sp^2 C-to-P bond length to the external sp^2 C of the aryl ring; the latter one is longer by 0.068 Å.

Also a strong indicator of delocalization is the shortening of the sp^2-sp^2 bond at C_3-C_4 as the double-bond character increases from the resonance interaction. The value for **3** is again the smallest one in the series (Table 3) and is in fact in the lower quartile of all those reported for the carbon−carbon double bond in organic compounds in a recent survey of structural data.[18] It should in particular be compared to the values[19] for the related parent 5-membered heterocycles pyrrole (1.417 Å), thiophene (1.423 Å), and furan (1.430 Å). The value for **3** is therefore smaller than that in these parents and in each case falls in the lower quartile (where q_1 is the cutoff value) established in a tabulation[18] of bond lengths for known structures containing each heterocyclic system (29 pyrroles, $q_1 = 1.401$ Å; 40 thiophenes, $q_1 = 1.415$ Å; 62 furans, $q_1 = 1.412$ Å). Since the C_3-C_4 bond is relatively remote from the P-aryl substituent, it is unlikely that nonbonded steric interactions are involved in this substantial bond shortening, and we attribute it to extensive electron delocalization in phosphole **3**.

Accompanying the shortening at the C_3-C_4 bond in 5-membered heterocycles should be some lengthening of the C_2-C_3 and C_4-C_5 bonds. The values for the above series are listed in Table 3. Going from the benzylphosphole[5] to **3**, the effect is not dramatic. It is not, however, inconsistent with values for other heterocycles, as can be seen by comparison to the values for the parent[19] (P) and to the lowest quartile[18] (q_1) of values for substituted heterocycles (58 pyrroles, $P = 1.382$ Å, $q_1 = 1.361$ Å; 60 thiophenes, $P = 1.370$ Å, $q_1 = 1.346$ Å; 125 furans, $P = 1.361$ Å, $q_1 = 1.329$ Å).

The effect of electron delocalization in aromatic systems on bond parameters can be expressed by an index developed by Bird.[20] Here, a heterocyclic system is placed on a scale where the fully delocalized benzene has a value of 100. The Bird index for furan is 43, for pyrrole 59, and for thiophene 66. Bird has also calculated a value of 35.5 for 1-benzylphosphole.[21] We

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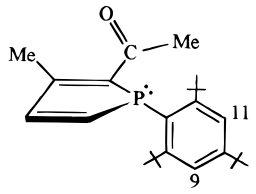
have calculated the value for our new phosphole **3** and find it to be considerably higher (56.5), in close proximity to the value for pyrrole and well above that for furan. On this basis, phosphole **3** can be considered as a legitimate member of the family of delocalized ("aromatic") 5-membered heterocycles, the first molecular phosphole to achieve this status.

The steric crowding in phosphole **3** is not without effect on the aryl substituent. The phosphole substituent on the *ipso* carbon causes considerable lengthening of the bond to the *ortho* ring carbons (Table 2), an effect which lessens the crowding of the *tert*-butyl substituents with the phosphole ring.

Examining P(III) pyramids generally, Schmidpeter et al. found that the sum of angles at phosphorus was informative; under the influence of bulky substituents, this sum may increase up to 344° from the normal value of 325°. On this scale, the sum of 331.7° for **3** suggests a moderate change in the pyramidality.[6b]

The pronounced electron delocalization in phosphole **3** could in principle reduce the reactivity of the phosphorus atom. The phosphole indeed showed resistance to air oxidation, allowing its handling in the atmosphere for several days. This stability may also come from the steric hindrance due to the presence of the *ortho tert*-butyl groups.

Electrophilic Substitution of Phosphole 3. While not itself a proof of aromaticity, it is a characteristic of aromatic heterocyclic systems that they undergo electrophilic substitution reactions. To the present, this is a reaction never observed with a phosphole, but we suspected that phosphole **3**, with its clear indication of extensive delocalization from the X-ray data, might well respond to such reactions. We chose to use Friedel−Crafts acylation as a model reaction, since this has been successfully applied to substitution on a phospholide ion moiety bonded in complexes with Mn[22] and Fe.[23] Refluxing **3** in petroleum ether with a small excess of acetyl chloride and aluminum chloride did indeed result in nearly complete consumption of the phosphole after 48 h. Analysis of the reaction mixture by ^{31}P NMR suggested that three new phospholes were formed (δ 8.3 (49%), δ 5.0 (22%), and δ 1.9 (22%)), with 7% of unreacted **3** present. The unreacted **3** was removed by silica gel chromatography, but attempts so far to separate the mixture of acylation isomers have not been successful. Spectral characterization therefore has been performed on the best fraction from chromatography (ratio 51:33:16, respectively). That the phospholes did indeed bear an acetyl group was demonstrated first by IR ($\nu_{C=O}$ = 1654 cm^{-1}) and by mass spectral analysis of the three-component mixture (M^+ = 384). The ^{1}H NMR spectrum contained readily recognized signals from the major component with ^{31}P NMR δ 8.3. The acetyl methyl was present as a doublet ($^4J_{PH}$ = 8.1; note again the very large size for four-bond coupling in this phosphole) at δ 2.48 and only two proton signals from the phosphole ring were present that were coupled by 6.9 Hz (as well as to ^{31}P). Hence, they were adjacent, allowing the assignment of structure **10** to this product. This orientation is just that expected from analogy with pyrrole chemistry; attack at the 2-position of 3-methylpyrrole is common on electrophilic substitution.[24] The ^{13}C NMR spectrum was also consistent with structure **10** (see Experimental Section). The other two phospholes are assigned structures **11** and **12**. The 5-acetyl isomer (**11**) with δ_P 5.0 was recognized from the large ^{31}P coupling to the carbonyl carbon (δ 193.8, J = 18.7), while the 4-acetyl isomer (**12**) with δ_P 1.9 had a much smaller coupling constant (δ 195.4, J = 7.1 Hz). Structure of the 5-acetyl isomer



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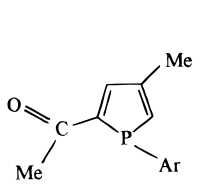
11 was also supported by the strongly deshielded signal for C$_4$−H at δ 7.65, which was split only by the phosphorus atom (23.9 Hz).



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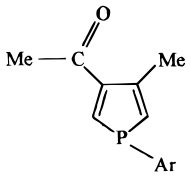

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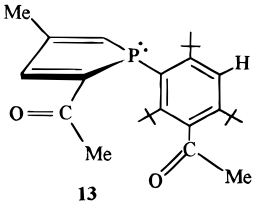
When the acylation was performed with approximately 2 equiv of acetyl chloride and $AlCl_3$, another product (**13**) was also formed in 44% along with 31% **10**, 9% **11**, and 16% **12**. Compound **13** with ^{31}P NMR δ 11.7 could be separated from the acetylphospholes by chromatography, but a sample of only 70% purity could be obtained due to decomposition. The mass spectrum showed that the compound was a diacetyl derivative (M^+ = 426). The ^{13}C spectrum revealed that the second acetyl group had entered the benzene ring, rather than the phosphole ring; only one aryl carbon (δ 123.9, J = 11.3 Hz, C$_{11}$) possessed a proton. In the phosphole ring, the carbonyl carbon had the large constant associated with two-bond coupling (24.0 Hz), indicating either a 2-acetyl or a 5-acetyl group. The proton NMR spectrum contained a signal at δ 7.82 which showed only splitting by ^{31}P (22.9 Hz), and none by an adjacent C−H. This eliminates the possibility of a 2-acetyl group, allowing the assignment of 5,9-diacetyl substitution to **13**.



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Experimental Section

General Considerations. The ^{31}P, ^{1}H, and ^{13}C NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 500, and 125.7 MHz, respectively. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV. All manipulations with air and moisture sensitive compounds, such as chlorophosphine **4** and phosphines **3**, **5**, and **10**−**13**, as well as phospholium salt **9** were performed under an atmosphere of nitrogen.

1-(2,4,6-Tri-*tert*-butylphenyl)-3-methyl-3-phospholene (5). A mixture of 18.5 g (0.0569 mol) of 1-bromo-2,4,6-tri-*tert*-butylbenzene[25] in 140 mL of dry THF was treated with 32.7 mL of a 2 M hexane solution of butyllithium at −78 °C. After 2 h of stirring, the aryllithium so obtained was slowly reacted with a solution of 7.65 g (0.0569 mol) of chlorophospholene **4**[26] in 30 mL of THF. After a 3 h stirring period at −78 °C, the mixture was allowed to warm to room temperature, and the contents of the flask were stirred overnight. Solvent was evaporated, and the residue suspended in 250 mL of *n*-hexane. Filtration of the suspension and evaporation of the filtrate afforded 19.1

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g (98%) of phosphine **5**: ^{31}P NMR ($CDCl_3$) δ 8.8; MS, *m*/*z* (rel intensity) 344 (M^+, 60), 343 (100), 329 (10), 288 (21), 276 (35), 261 (29), 220 (47), 205 (15), 99 (17), 57 (45); HRMS calcd for $C_{23}H_{37}P$ 344.2633, found 344.2701.

1-(2,4,6-Tri-*tert*-butylphenyl)-3-methyl-3-phospholene 1-Oxide (6). A solution of 15.0 g (0.0436 mol) of phosphine **5** in 100 mL of chloroform was slowly treated with 6.0 mL (0.0528 mol) of 30% hydrogen peroxide at 0 °C with intensive stirring. After a period of 1 h, the mixture was washed with 4 × 30 mL of water. The organic phase was dried ($MgSO_4$), and the solvent was evaporated to give crude **6**. Column chromatography (silica gel, 3% methanol in chloroform) furnished 9.1 g of oxide **6** in a purity of 95% (yield 55%): ^{31}P NMR ($CDCl_3$) δ 58.6; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9H, *p*-CMe_3), 1.49 (s, 18H, *o*-CMe_3), 1.74 (s, 3H, C_3CH_3), 2.63−2.93 (m, 4H, CH_2), 5.42 (d, $^3J_{PH}$ = 30.8 Hz, 1H, CH═), 7.28 (m, 2H, ArH); MS, *m*/*z* (rel intensity) 360 (M^+, 9), 359 (13), 345 (5), 303 (100), 57 (61); HRMS calcd for $C_{23}H_{37}OP$ 360.2582, found 360.2619.

3,4-Dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphospholane 1-Oxide (7). To 17.4 g (0.0482 mol) of phospholene oxide **6** in 120 mL of chloroform was added dropwise 2.48 mL (0.0482 mol) of bromine in 20 mL of chloroform at 0 °C. After the addition, the contents of the flask were stirred at room temperature for 1.5 h. The crude product obtained after evaporation of the volatile components was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 18.8 g (75%) of dibromide **7** as a mixture of two diastereomers: ^{31}P NMR ($CDCl_3$) δ 49.8 for the major (90%) and 44.8 for the minor (10%) isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9H, *p*-CMe_3), 1.49 (s, 18H, *o*-CMe_3), 2.02 (s, 2.7H, C_3CH_3 (major)), 4.40 (m, 1H, CH) 7.31 (s, 2H, ArH); ^{13}C NMR (major isomer) δ 31.0 ($C_{4'}C(\underline{C}H_3)_3$), 32.0 ($^3J_{PC}$ = 8.0 Hz, C_3CH_3), 33.4 ($C_{2'}C(\underline{C}H_3)_3$), 34.4 ($C_{4'}\underline{C}Me_3$), 40.3 ($C_{2'}\underline{C}Me_3$), 46.2 ($^1J_{PC}$ = 70.0 Hz, C_5), 50.1 ($^1J_{PC}$ = 70.2 Hz, C_2), 57.6 ($^2J_{PC}$ = 4.8 Hz, C_4), 67.0 ($^2J_{PC}$ = 7.5 Hz, C_3), 123.9 ($^3J_{PC}$ = 13.2 Hz, $C_{3'}$), 126.5 ($^1J_{PC}$ = 108.2 Hz, $C_{1'}$), 152.9 ($C_{4'}$), 158.0 ($^2J_{PC}$ = 8.7 Hz, $C_{2'}$); CI-MS, 519 (M + H); MS, *m*/*z* (rel intensity) 461 (M − 57, 44), 381 (22), 303 (83), 231 (100), 57 (98).

Attempted Deoxygenation of Dibromophospholane Oxide 7. The reaction of dibromide **7** with 1.2 equiv of trichlorosilane and 3 equiv of pyridine in boiling benzene was carried out as described in the preparation of the triisopropylphenylphosphole **2**.[9] Due to extensive decomposition of **7**, resulting in, for example, the formation of tri-*tert*-butylbenzene, none of the expected phospholane **8** was obtained. Traces (ca. 5%) of phosphole **3** could be detected.

1-(2,4,6-Tri-*tert*-butylphenyl)-3-methylphosphole (3). To 10.0 g (0.0291 mol) of phospholene **5** in 400 mL of n-hexane was added 1.50 mL (0.0291 mol) of bromine in 25 mL of dichloromethane at 0 °C, over a period of 1 h. After the addition, the mixture was stirred at room temperature for 1.5 h. The 1-bromo-1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphospholium bromide (**9**) appeared as a yellow precipitate.

The suspension of the phospholium salt **9** so obtained was treated with a solution of 6.3 mL (0.0636 mol) of 2-picoline in 25 mL of dichloromethane at room temperature. After 1 h of stirring, the mixture darkened. The stirring was continued for an additional 20 h. Then, the volatile components were removed by vacuum distillation and the solid material remaining in the bottom of the flask was extracted with 4 × 100 mL of *n*-hexane. The crude product obtained after removing the solvent *in vacuo* was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 6.50 g of phosphole **3** in a purity of 95% (yield 62%). Recrystallization from acetone yielded 3.5 g (35%) of **3**: mp 102−104 °C; ^{31}P NMR ($CDCl_3$) δ −0.40; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9H, *p*-CMe_3) 1.40 (s, 18H, *o*-CMe_3), 2.24 (d, $^4J_{PH}$ = 7.3 Hz, 3H, C_3CH_3), 6.53 (d(b), $^2J_{PH}$ = 36.1 Hz, 1H, C_2H), 6.69 (dd, $^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, C_4H), 6.93 (ddd, $^2J_{PH}$ = 32.9 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, C_5H), 7.48 (s, 1H, ArH), 7.49 (s, 1H, ArH); ^{13}C NMR, see Table 1; MS, *m*/*z* (rel intensity) 342 (M^+, 100), 327 (83), 285 (24), 57 (33). Anal. Calcd for $C_{23}H_{35}P$: C, 80.70; H, 10.23. Found: 80.49; H, 10.08.

Monoacetylation of Phosphole 3. A mixture of 1.0 g (2.92 mmol) of phosphole **3**, 0.47 g (3.52 mmol) of aluminum chloride, and 0.35 mL (4.92 mmol) of acetyl chloride in 50 mL of 40−70 °C petroleum ether was refluxed with stirring for 48 h. Volatile components were evaporated, and the residue was taken up in 50 mL of chloroform. The mixture was treated with 10 mL of water, and the organic phase was dried ($MgSO_4$). Evaporation of the solvent left an oil containing 93% of acetylphospholes (**10** (49%), **11** (22%), and **12** (22%)) and 7% of unreacted **3** according to ^{31}P NMR. Column chromatography (silica gel, 2% methanol in chloroform) afforded a fraction (0.24 g) containing 51% of **10**, 33% of **11**, and 16% of **12**: MS, *m*/*z* (rel intensity) 384 (M^+, 49), 369 (M − Me, 40), 341 (M − Ac, 49), 231 (24), 57 (100); HRMS calcd for $C_{25}H_{37}OP$ 384.2582, found 384.2641.

10: ^{31}P NMR ($CDCl_3$) δ 8.3; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, *p*-CMe_3), 1.37 (s, *o*-CMe_3), 1.54 (d, $^4J_{PH}$ = 2.0 Hz, C_3CH_3), 2.48 (d, $^4J_{PH}$ = 8.1 Hz, $C(O)CH_3$), 6.79 (dd, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.9, C_4H), 7.26 (dd, $^2J_{PH}$ = 30.1 Hz, $^3J_{HH}$ = 6.9 Hz, C_5H), 7.49 (s, ArH), 7.50 (s, ArH); ^{13}C NMR ($CDCl_3$) δ 18.8 (s, $C_3\underline{C}H_3$), 30.7 (s, $C(O)\underline{C}H_3$), 119.4 (s, C_9), 123.3 (d, $^3J_{PC}$ = 10.5 Hz, C_{11}), 132.6 (d, $^2J_{PC}$ = 15.1 Hz, C_4),* 134.2 (d, $^1J_{PC}$ = 12.3 Hz, C_5),* 195.3 (d, $^2J_{PC}$ = 25.6 Hz, C═O) (the asterisk indicates may be reversed).

11: ^{31}P NMR ($CDCl_3$) δ 5.0; ^{1}H NMR ($CDCl_3$) δ 1.88 (C_3CH_3), 2.28 (d, $^4J_{PH}$ = 6.3 Hz, $C(O)CH_3$), 6.54 (d(b), $^2J_{PH}$ = 35.4 Hz, C_2H), 7.53 (s, ArH), 7.54 (s, ArH), 7.65 (dd, $^3J_{PH}$ = 23.9 Hz, $^4J_{HH}$ = 2.3 Hz, C_4H); ^{13}C NMR ($CDCl_3$) δ 19.9 (d, $^3J_{PC}$ = 8.2, C_3CH_3), 193.8 (d, $^2J_{PC}$ = 18.7, C═O).

12: ^{31}P NMR ($CDCl_3$) δ 1.9; ^{1}H NMR ($CDCl_3$) δ 1.54 (d, $^4J_{PH}$ = 2.0 Hz, C_3CH_3), 2.47 (s, $C(O)CH_3$), 6.93 (d, $^2J_{PH}$ = 32.0 Hz, C_2H), C_5H overlapped, 7.51 (s, ArH), 7.52 (s, ArH); ^{13}C NMR ($CDCl_3$) δ 18.6 (d, $^3J_{PC}$ = 3.9 Hz, C_3CH_3), 195.4 (d, $^3J_{PC}$ = 7.1 Hz, C═O).

Diacetylation of Phosphole 3. In the above reaction mixture, the use of twice as much acetyl chloride (0.6 mL, 8.4 mmol) added in two portions resulted in a mixture containing 31% of **10**, 9% of **11**, 16% of **12**, and 44% of **13**. Column chromatography (as above) afforded 0.15 g (8%) of **13** in a purity of 70%: ^{31}P NMR δ 11.7; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, *p*-CMe_3), 1.39 (s, *o*-CMe_3), 1.67 (d, $^4J_{PH}$ = 1.7 Hz, C_3CH_3), 2.55 (s, 9-$C(O)CH_3$), 2.66 (d, $^4J_{PH}$ = 8.6 Hz 5-$C(O)CH_3$), ∼7.3 (d, partially overlapped, C_2H), 7.53 (s, ArH), 7.82 (d, $^3J_{PH}$ = 22.9 Hz, C_4H); ^{13}C NMR ($CDCl_3$) δ 17.2 (s, C_3CH_3), 30.9 (s, $C_5C(O)\underline{C}H_3$),* 29.3 (s, $C_9C(O)\underline{C}H_3$),* 123.7 (d, J_{PC} = 11.3 Hz, C_{11}), 195.6 (d, $^2J_{PC}$ = 24.0 Hz, $C_5\underline{C}(O)CH_3$), 196.2 (d, $^4J_{PC}$ = 6.7 Hz, $C_9\underline{C}(O)CH_3$) (the asterisk indicates may be reversed; GC-MS, *m*/*z* (rel intensity) 426 (M^+, 29), 411 (M − Me, 19), 383 (M − Ac, 43), 231 (33), 57 (100); HRMS calcd for $C_{27}H_{39}O_2P$ 426.2688, found: 426.2656.

X-ray Structure Analysis of $C_{23}H_{35}P$ (3). Unit cell dimensions: a = 21.137(4) Å, b = 22.327(5) Å, c = 9.149(2) Å, V = 4318(2) Å^3, Z = 8, orthorombic, space group *Pbca*, d = 1.054 g cm^{-3}, R = 0.0729.

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Supporting Information Available: Crystallographic experimental details, coordinates, bond lengths and angles, and anisotropic displacement coefficients, together with H atom coordinates and isotropic displacement coefficients (8 pages). See any current masthead page for ordering and Internet access instructions.

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