

# Phospholes with reduced pyramidal character from steric crowding III NMR and X-ray diffraction studies on 1-(2,4,6-tri-isopropylphenyl)-3-methylphosphole

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## Abstract

The 2,4,6-tri-isopropylphenyl substituent was placed on the phosphorus of a phosphole to reduce the pyramidal character. That this was accomplished was revealed by single crystal X-ray diffraction analysis; with respect to the plane of C<sub>2</sub>–P–C<sub>5</sub> in the phosphole ring, the *ipso* carbon of the benzene ring was deflected by only 58.0°, whereas the deflection is 66.9° in the uncrowded 1-benzylphosphole. This proves that the concept of reducing the pyramidal character (with the goal of increasing the electron delocalization) through steric crowding can be realized. In the crystal the two rings are in orthogonal planes, but this relation is not retained in solution; NMR studies show that the two edges of the benzene ring, as well as the 2,6-isopropyl groups, are identical.

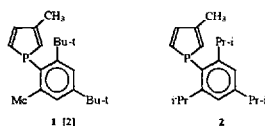
**Keywords:** Phosphole; Single crystal X-ray analysis; Stereostructure; Delocalization; Aromaticity; Bird-index

## 1. Introduction

Theoretical calculations [1] have suggested that as the phosphorus atom in a phosphole approaches planarity from its normal pyramidal state, the extent of delocalization of the lone pair into the  $\pi$  system should increase. We are engaged in a program to test this idea experimentally, and to this end we first synthesized a phosphole [1-(2,4-di-*tert*-butyl-6-methylphenyl)-3-methylphosphole **1**] with a large, sterically demanding substituent on phosphorus that might interact with the phosphole ring and cause partial flattening of the phosphorus atom [2]. This phosphole **1** proved to be a solid, but crystals suitable for X-ray diffraction analysis, which would have provided confirmation of the flattening as well as delocalization through changes in bond lengths,

could not be obtained. However, the photoelectron spectrum of phosphole **1** provided an indication that there was increased electron delocalization relative to other phospholes for which data are available [3]. Phosphole **1** had a band for ionization of the lone pair on phosphorus at 7.9 eV, the lowest value ever recorded for a phosphole. Furthermore, the value was 0.35 eV higher than for the tetrahydro derivative; in all other known phospholes, the lone pair ionization energy is the same as in the tetrahydro derivatives, which has been taken to mean that there is rather little electron delocalization in such phospholes. In continuing these studies we have succeeded in synthesizing a new, sterically congested phosphole **2** with a 2,4,6-tri-isopropylphenyl P-substituent that did give crystals amenable to structure determination by X-ray diffraction analysis. This has allowed us to obtain direct experimental confirmation that a large P-substituent can indeed cause partial flattening of the phosphorus atom. Our experimental results are presented in this paper.

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## 2. Results and discussion

### 2.1. Synthesis and NMR spectral properties of phosphole 2

The synthesis of phosphole **2** was accomplished by the same sequence of reactions as used in our previous work [2] (Scheme 1). All reactions proceeded smoothly in good yield. Phosphole **2** was obtained analytically pure by column chromatography and recrystallization from acetone. The  $^{31}\text{P}$  NMR shift of **2** ( $\delta_p = -8.6$ ) was somewhat upfield of that for the uncrowded 1-phenylphosphole ( $\delta_p = 7.8$  [4]); the upfield shifting may arise from steric interactions of the  $\gamma$ -related *ortho* isopropyl carbons. Increased electron delocalization is predicted from theoretical calculations to cause deshielding [1], although no experimental verification of this prediction is yet possible. The value for **2** should also be compared with that for phosphole **1** ( $\delta_p = 1.8$ ). As additional crowded phospholes become available, the competing effects of steric crowding and increased electron delocalization should become more understandable.

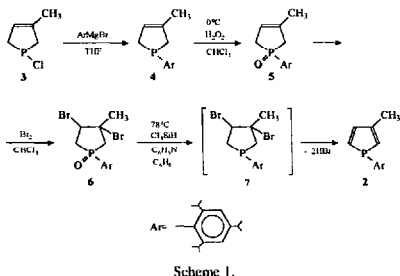
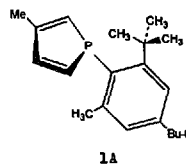
Phosphole **2** was also characterized by mass spectrometry. As is typical of phospholes, the molecular ion was the base peak in the spectrum.

In our earlier studies of phosphole **1**, it was deduced from the  $^{13}\text{C}$  NMR spectrum that the 2,4-di-*tert*-butyl-6-methylphenyl ring was fixed in a plane orthogonal to the phosphole ring, as shown in structure **1A**. The sterically controlled  $^{31}\text{P}$ - $^{13}\text{C}$  two-bond and three-bond coupling constants were significantly larger for carbons

Table 1  
 $^{13}\text{C}$  NMR data for phosphole **2** in  $\text{CDCl}_3$  solution

	$\delta$	$J_{\text{PC}}$ (Hz)
$\text{C}_2$	128.1	—
$\text{C}_3$	143.3	16.0
$\text{C}_4$	136.1	14.4
$\text{C}_5$	135.2	—
$\text{C}_1$ -Me	18.8	3.6
$\text{C}_2'$	156.8	14.1
$\text{C}_3'$	121.6	5.5
$\text{C}_4'$	151.5	—
$\text{C}_2'$ - $\text{CH}(\text{CH}_3)_2$	24.9	—
$\text{C}_3'$ - $\text{CH}(\text{CH}_3)_2$	23.8	—
$\text{C}_2'$ - $\text{CHMe}_2$	31.5	16.0
$\text{C}_4'$ - $\text{CHMe}_2$	34.3	—

of the substituent held closer to the lone pair on phosphorus. The barrier to rotation (or to pyramidal inversion, which would have the same effect) was substantial, since the spectrum was unchanged at  $100^\circ\text{C}$ . A feature of the  $^1\text{H}$  NMR spectrum supported this conformational assignment: a five-bond coupling constant for  $^{31}\text{P}$  to the methyls of the 2-*tert*-butyl group could be detected (2 Hz), as would only occur if this group were in close proximity to the lone pair.



Scheme 1.

Table 2  
 $^1\text{H}$  NMR data for phosphole **2** in  $\text{CDCl}_3$  solution

	$\delta$		$J_{\text{PH}}$ (Hz)	$^3J_{\text{HH}}$ (Hz)	$^4J_{\text{HH}}$ (Hz)
$\text{C}_2$ -H	6.60	m	38.8	—	—
$\text{C}_3$ -H	6.84	ddd	17.0	7.0	1.0
$\text{C}_4$ -H	7.05	ddd	35.8	7.0	2.3
$\text{C}_5$ - $\text{CH}_3$	2.23	d	5.1	—	—
$\text{C}_1$ -H	6.99	d	—	—	3.2
$\text{C}_2'$ - $\text{CH}(\text{CH}_3)_2$	1.24 <sup>a</sup>	d	—	7.0	—
$\text{C}_3'$ - $\text{CH}(\text{CH}_3)_2$	1.15 <sup>a</sup>	d	—	6.9	—
$\text{C}_2'$ - $\text{CHMe}_2$	3.11	m	—	6.7	—
$\text{C}_4'$ - $\text{CHMe}_2$	2.86	septet	—	6.9	—

<sup>a</sup> May be reversed.

Table 3  
Positional parameters and  $B_{eq}$  for phosphole 2

Atom	x	y	z	$B_{eq}$
P(1)	0.4351(2)	0.16567(5)	0.67507(8)	1.82(2)
C(2)	0.2951(7)	0.1298(2)	0.5700(3)	2.19(9)
C(3)	0.4439(7)	0.1006(2)	0.5226(3)	2.00(8)
C(4)	0.6645(7)	0.0972(2)	0.5754(3)	2.14(9)
C(5)	0.6841(7)	0.1248(2)	0.6648(3)	2.12(9)
C(6)	0.390(1)	0.0721(2)	0.4210(3)	3.4(1)
C(7)	0.2948(6)	0.1482(2)	0.7855(3)	1.55(7)
C(8)	0.2166(7)	0.1955(2)	0.8392(3)	1.81(8)
C(9)	0.0980(7)	0.1842(2)	0.9205(3)	1.93(8)
C(10)	0.0581(7)	0.1283(2)	0.9521(3)	1.84(8)
C(11)	0.1381(7)	0.0825(2)	0.8995(3)	1.82(8)
C(12)	0.2551(6)	0.0909(2)	0.8170(3)	1.63(8)
C(13)	0.2478(8)	0.2589(2)	0.8110(3)	2.33(9)
C(14)	0.023(1)	0.2857(2)	0.7743(5)	4.9(2)
C(15)	0.366(1)	0.2936(2)	0.8958(4)	4.1(1)
C(16)	-0.0710(7)	0.1175(2)	1.0412(3)	2.04(9)
C(17)	-0.3045(8)	0.1444(3)	1.0290(4)	3.4(1)
C(18)	0.0632(8)	0.1390(2)	1.1366(3)	2.53(10)
C(19)	0.3349(7)	0.0372(2)	0.7647(3)	1.82(8)
C(20)	0.1401(8)	0.0303(2)	0.7307(3)	2.66(10)
C(21)	0.5172(8)	0.0052(2)	0.8313(3)	2.9(1)

In the new phosphole 2, the  $^{13}\text{C}$  chemical shifts and  $^{13}\text{C}$ – $^{31}\text{P}$  coupling constants would be expected to differ for the carbons on the two edges of the benzene ring if the steric crowding prevented rotation around the C–P bond. However, the spectrum contained only one signal for the *ortho* ring carbons, as well as for the 2,6-isopropyl groups (Table 1). This can only mean that the crowding is not severe enough to prevent rotation around the P–C bond (or inversion of the phosphorus pyramid).

The  $^1\text{H}$  NMR spectrum (Table 2) of phosphole 2 provided confirmation of this conclusion; the 2- and 6-isopropyl groups were identical. Furthermore, there was no observable four-bond coupling of phosphorus to  $\text{C}_3$ –H, that is not fixed in proximity to the lone pair.

We have employed the PM3 semi-empirical molecular orbital method within the Mopac 93 program (Fujitsu Ltd.) to gain an understanding of the failure of the isopropyl groups to prevent the rotation (or inversion) at phosphorus. The PM3 method is particularly well suited to computation of phosphorus-containing systems [5].

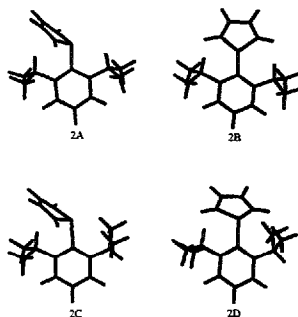
Table 4  
Bond lengths (Å) and angles (°) for phospholes 2 and 8

Atoms	2	8 [6]
P <sub>1</sub> –C <sub>2</sub>	1.782(4)	1.786(5)
P <sub>1</sub> –C <sub>5</sub>	1.778(4)	1.780(4)
P <sub>1</sub> –C <sub>3</sub> <sup>a</sup>	1.835(6)	1.858(4)
C <sub>2</sub> –C <sub>3</sub>	1.340(6)	1.343(6)
C <sub>3</sub> –C <sub>4</sub>	1.436(6)	1.438(6)
C <sub>4</sub> –C <sub>5</sub>	1.366(6)	1.343(7)
C <sub>2</sub> –P <sub>1</sub> –C <sub>3</sub> <sup>a</sup>	109.6(2)	106.1(2)
C <sub>5</sub> –P <sub>1</sub> –C <sub>3</sub> <sup>a</sup>	113.7(2)	105.9(2)
C <sub>5</sub> –P <sub>1</sub> –C <sub>2</sub>	91.1(2)	90.7(2)

<sup>a</sup> C<sup>\*</sup> = C<sub>7</sub> for 2, C<sup>\*</sup> = C<sub>8</sub> for 8.

Using three different starting geometries for both the isopropyl groups, we calculated the geometry optimized energy surface for the rotation of the phosphole ring about the aryl ring in each case. This would give us information regarding the energy differences between a substantial number of conformers along the phosphole ring rotation pathway.

In one case we used the conformer with the methine protons of both the isopropyl groups closest to the phosphole ring (2A). Comparison of all the heats of formation showed this to be the most stable form, with a heat of formation of 42.0 kcal mol<sup>-1</sup>. Rotation of the phosphole ring about the aryl ring caused the energy to increase to a maximum of 45.9 kcal mol<sup>-1</sup> at the conformer in which the phosphole ring is midway between the geometry shown in 2A and that where the phosphole ring is rotated by 180° (2B). As will be seen in the next section, the calculated low-energy conformation (2A) is that adopted in the crystalline form of phosphole 2, as determined by X-ray analysis.



In the second case, one of the isopropyl groups in 2A (*exo*) was rotated by 180°, so that the two methyl groups were closer to the phosphole ring (2C). This increased the heat of formation to 48.3 kcal mol<sup>-1</sup>. As in the previous case, the ring–ring torsion energy surface was studied computationally. An energy maximum (54.8 kcal mol<sup>-1</sup>) occurred when the phosphole ring was midway between the starting geometry and the conformer where the phosphole ring was rotated by 180° (2D).

In the third case, both isopropyl groups in 2A were rotated by 180° so that the methyl groups were close to the phosphole ring. This resulted in an energy surface with much higher heats of formation (56.8–61.2 kcal mol<sup>-1</sup>). It can reasonably be assumed that 2

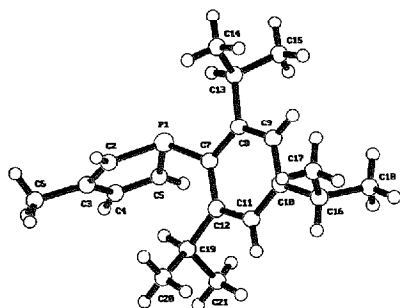
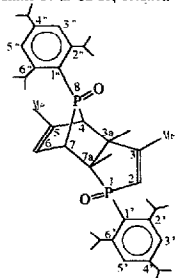
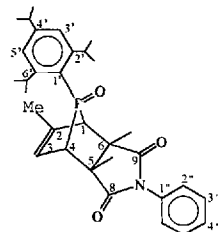


Fig. 1. Crystal structure of phosphole 2.

Table 5  
<sup>13</sup>C NMR data for dimer 10 in CDCl<sub>3</sub> solution

	$\delta$	$J_{P,C}$ (Hz)	$J_{P,C}$ (Hz)
C <sub>2</sub>	130.7	97.9	
C <sub>3</sub>	157.1	23.9	9.1
C <sub>3a</sub>	51.9	13.1	13.1
C <sub>1</sub>	52.6		64.5
C <sub>7</sub>	135.8		12.2
C <sub>7e</sub>			
C <sub>7</sub>	48.0		60.0
C <sub>3a</sub>	43.5	74.8	12.8
C <sub>3</sub> -CH <sub>3</sub> <sup>b</sup>	18.9	16.7	
C <sub>5</sub> -CH <sub>3</sub> <sup>b</sup>	19.3		
C <sub>1</sub> <sup>f</sup>	127.7	97.9	
C <sub>1</sub> <sup>f</sup>	127.7		97.9
C <sub>3</sub> <sup>f</sup>	152.8	9.5	
C <sub>3</sub> <sup>f</sup> , C <sub>6</sub> <sup>f</sup> , C <sub>5</sub> <sup>f</sup>			
C <sub>3</sub> <sup>f</sup> , C <sub>5</sub> <sup>f</sup> , C <sub>5</sub> <sup>g</sup>			
C <sub>1</sub> <sup>e</sup>	151.4		
C <sub>7</sub> <sup>e</sup>	150.8		
ortho-CH(CH <sub>3</sub> ) <sub>2</sub>	23.4		
para-CH(CH <sub>3</sub> ) <sub>2</sub>	25.3		
ortho-CHMe <sub>2</sub>	31.7		
para-CHMe <sub>2</sub>	33.9		

<sup>a</sup> Overlapped in the range  $\delta = 119.9$ – $124.5$ .<sup>b,c</sup> May be reversed.<sup>d</sup> Overlapped in the range  $\delta = 149.9$ – $152.0$ .<sup>e</sup> May be reversed.Table 6  
<sup>13</sup>C NMR for Diels-Alder cycloadduct 11 in CDCl<sub>3</sub> solution

	$\delta$	$J_{PC}$ (Hz)
C <sub>1</sub>	51.1	63.2
C <sub>2</sub>	140.7	11.4
C <sub>3</sub>	121.9	10.5
C <sub>4</sub>	48.3	63.6
C <sub>5</sub> <sup>a</sup>	43.5	13.8
C <sub>6</sub> <sup>a</sup>	44.8	15.4
C <sub>1</sub> <sup>b</sup>	175.7	14.4
C <sub>2</sub> <sup>b</sup>	175.5	13.6
C <sub>3</sub> -CH <sub>3</sub>	19.1	—
C <sub>1</sub> <sup>c</sup>	120.9	94.1
C <sub>2</sub> <sup>c</sup>	153.1	10.4
C <sub>3</sub> <sup>c</sup>	122.4	9.7
C <sub>4</sub> <sup>c</sup>	152.6	2.1
C <sub>5</sub> <sup>c</sup>	121.4	10.2
C <sub>6</sub> <sup>c</sup>	151.9	9.8
C <sub>1</sub> -CH(CH <sub>3</sub> ) <sub>2</sub> , C <sub>6</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	23.5	
C <sub>3</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	26.1	
C <sub>2</sub> -CHMe <sub>2</sub> , C <sub>5</sub> -CHMe <sub>2</sub>	32.3	6.1
C <sub>4</sub> -CHMe <sub>2</sub>	34.1	
C <sub>1</sub> <sup>d</sup>	131.7	
C <sub>2</sub> <sup>d</sup>	126.4	
C <sub>3</sub> <sup>d</sup>	129.1	
C <sub>4</sub> <sup>d</sup>	128.7	

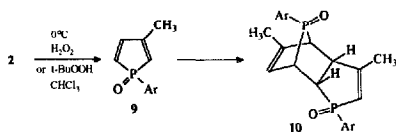
<sup>a-c</sup> May be reversed.

will not seek to adopt any of these energetically unfavorable conformations.

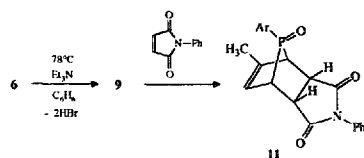
From the second case, we see that the energy difference between the low energy and high energy conformers is 6.6 kcal mol<sup>-1</sup>. If it is assumed that  $\Delta S^\ddagger$  is the same for both conformers, then the differences in heats of formation for 2A  $\rightarrow$  2B and 2C  $\rightarrow$  2D are approximations of the free energy of activation for rotation. If the barrier to rotation has not been severely underestimated, it is small enough to allow the rotation to occur under the experimental temperatures used in the NMR studies. This supports our observations, which are consistent with just such a rotation.

## 2.2. Crystal structure of phosphole 2

X-ray diffraction analysis of a single crystal of phosphole 2 was performed at  $-150^\circ\text{C}$ . The molecular

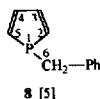


Scheme 2. Ar as in Scheme 1.



Scheme 3. Ar as in Scheme 1.

structure that was established is shown in Fig. 1, while the positional parameters are listed in Table 3. It is seen that the phosphole ring and the benzene ring lie in orthogonal planes, just as deduced for phosphole **1** in solution from NMR spectroscopic studies. In this conformation, the two edges of the benzene ring, as well as the 2,6-isopropyl groups, are non-equivalent, and if this conformation were retained in solution, these carbons would have different chemical shifts and coupling constants. As noted in the preceding section, this is not the case, indicating that the energy barrier to rotation around the P–C bond, or the pyramidal inversion barrier, is not as high as in phosphole **1**. Nevertheless, substantial steric crowding is present, and the desired flattening effect on the phosphorus pyramid is clearly evident. This is revealed by a comparison of appropriate geometric properties with those of 1-benzylphosphole (**8**) [6], as an example of a relatively uncrowded phosphole.



In one view, the deflection of the *ipso* carbon ( $C_7$ ) of the benzene ring from the plane established by  $C_2$ –P– $C_5$  of the phosphole ring is a measure of the

flattening. The angle of deflection in benzylphosphole is  $66.9^\circ$ , but in phosphole **2** this angle is diminished to  $58.0^\circ$ . The calculated angle using the PM3 semi-empirical program is a not unreasonable value of  $62.80$ . Another indication of the distortion at phosphorus comes from an analysis of the least-squares planes through selected groups of atoms. We define plane 1 as including P– $C_2$ – $C_3$ – $C_4$ – $C_5$  (mean standard deviation for **2**  $0.006 \text{ \AA}$ ;  $0.058 \text{ \AA}$  for **8**), and plane 2 as including  $C_2$ – $C_1$ – $C_3$ – $C_5$  (mean standard deviation  $0.0022 \text{ \AA}$  for **2**;  $0.0017 \text{ \AA}$  for **8**). The exocyclic carbon on P lies below plane 1 by  $1.617 \text{ \AA}$  for benzylphosphole, but only  $1.456 \text{ \AA}$  for **2**. The planarity of the phosphole ring is defined by the deflection of P from plane 2; for **2**, the deflection is  $0.276 \text{ \AA}$ , and for **8**,  $0.237 \text{ \AA}$ , indicating reduced planarity in the more crowded **2**. This feature was also revealed by the larger interplanar angle measured between plane 1 and plane 2 for **2** ( $7.59^\circ$ ) than for benzylphosphole (**8**) ( $4.92^\circ$ ).

A comparison of selected bond lengths and bond angles in the two phospholes (**2** and **8**) is provided in Table 4. It is seen that there is only a slight difference in lengths for P to the ring carbons. The exocyclic P–C bond is, however, significantly shorter in **2** than in benzylphosphole **8**, which can largely be attributed to the  $sp^2$  hybridization at carbon in the former, and  $sp^3$  in the latter. There is no significant difference in the  $C_3$ – $C_4$  single bond length, which indicates little difference in the electron delocalization of the two com-

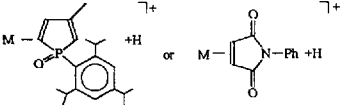
Table 7

$^1\text{H}$  NMR data for dimer **10** and Diels–Alder cycloadduct **11** in  $\text{CDCl}_3$  solution

	<b>10</b> $\delta$ (mult., $J$ (Hz), integral)	<b>11</b>
<i>ortho</i> - $\text{CH}(\text{C}_6\text{H}_5)_2$	1.20–1.28 (m, 24H)	1.24 (d, $J = 6.9$ , 6H) 1.28 (d, $J = 6.6$ , 6H)
<i>para</i> - $\text{CH}(\text{C}_6\text{H}_5)_2$	1.34–1.39 (m, 12H)	1.33 (d, $J = 6.6$ , 3H) 1.42 (d, $J = 6.6$ , 3H)
$\text{C}_5$ –Me	1.61 (s, 3H)	$\text{C}_2$ –H
$\text{C}_3$ –Me	2.00 (s, 3H)	1.67 (s, 3H)
$\text{CHMe}_2$	2.86 (m, 2H) 3.34 (sept, $J = 6.6$ , 2H) 3.62 (sept, $J = 6.6$ , 2H)	2.88 (sept, $J = 6.8$ , 1H) 3.30 (sept, $J = 6.5$ , 1H) 3.52 (sept, $J = 6.3$ , 1H)
$\text{C}_6$ –H	6.17 (d, $J = 12.4$ ) <sup>a</sup>	$\text{C}_1$ –H
$\text{C}_2$ –H	6.23 (d, $J = 23.9$ ) <sup>a</sup>	5.84 (d, $J = 6.6$ , 1H)
ArH	6.99–7.08 (m, 4H)	7.02–7.48 (m, 7H)

<sup>a</sup> Total intensity 2H.

Table 8  
Mass spectral data for dimer **10** and Diels–Alder cycloadduct **11**

Compound	<b>10</b>	<b>11</b>
	<i>m/z</i> (rel. int.) (%)	
M <sup>+</sup>	632 (51)	489 (51)
M – Me <sup>++</sup>	617 (3)	474 (5)
M – [2,4,6-tri- <sup>1</sup> PrC <sub>6</sub> H <sub>3</sub> PO] <sup>++</sup>	382 (18) <sup>a</sup>	239 (18) <sup>b</sup>
M – [2,4,6-tri- <sup>1</sup> PrC <sub>6</sub> H <sub>3</sub> PO–Me] <sup>++</sup>	367 (14)	
	317 (100)	317 (62)
317 – H <sup>++</sup>		
2,4,6-tri- <sup>1</sup> PrC <sub>6</sub> H <sub>3</sub> PO <sup>++</sup>	316 (75)	316 (28)
250 – Me <sup>++</sup>	250 (8)	250 (100) <sup>c</sup>
	235 (9)	235 (69)
		92 (61) <sup>d</sup>

<sup>a</sup> 381 (25); <sup>b</sup> 240 (54); <sup>c</sup> 251 (52); <sup>d</sup> PhN + H.

pounds (**2** and **8**). The C<sub>2</sub>–C<sub>3</sub> and C<sub>4</sub>–C<sub>5</sub> double bonds in **2** do have an averaged length that is slightly longer (0.01 Å) than the averaged value for benzylphosphole (**8**), but this is not too significant.

To have an exact indicator of aromaticity, the Bird-index [7] of phosphole **2** was also calculated. Phosphole **2** exhibited a Bird-index of 40.4, which is somewhat bigger than the value of 35.3 reported for benzylphosphole **8** [7].

We conclude that the steric crowding in **2** causes some flattening at phosphorus, but the electron delocalization is increased only to a slight extent.

### 2.3. Synthesis and spectral characterization of the dimer and a Diels–Alder adduct of the oxide of phosphole **2**

To complete the characterization of phosphole **2**, its conversion to the oxide **9** was performed by the action of hydrogen peroxide (Scheme 2). Phosphole oxide **9** could only be observed as a transient species by <sup>31</sup>P NMR spectroscopy when the oxidation was performed at about 0°C; it had a shift of δ<sub>p</sub> = 49.2, but rapidly formed the Diels–Alder dimer **10**, as is characteristic of phosphole oxides.

The phosphole oxide was also generated by the dehydrobromination of dibromophospholane oxide **6** (Scheme 3). In this case the oxide was trapped upon formation with N-phenylmaleimide, giving the Diels–Alder adduct **11**.

The phosphanorbornene derivatives **10** and **11** were characterized by <sup>13</sup>C NMR (Tables 5 and 6), <sup>1</sup>H NMR (Table 7) and mass spectral (Table 8) data. The spectral features are consistent with those reported for related

dimers, and show no special effects from the steric crowding at phosphorus.

### 3. Experimental details

FT <sup>31</sup>P NMR spectra were recorded with an IBM NR-80 spectrometer using 85% H<sub>3</sub>PO<sub>4</sub> as external standard with CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Bruker DRX 500 and IBM NR-80 instruments respectively, with Me<sub>4</sub>Si as internal standard. The coupling constants are given in hertz. Mass spectra were obtained on an MS 25-RFA spectrometer at 70 eV.

#### 3.1. 3-Methyl-1-(2,4,6-tri-isopropylphenyl)3-phosphole 1-oxide (**5**)

A solution of 0.183 mol of 2,4,6-tri-isopropylphenylmagnesium bromide in THF (prepared from 4.4 g (0.183 mol) of magnesium and 51.8 g (0.183 mol) of 1-bromo-2,4,6-tri-isopropylbenzene <sup>1</sup> in 140 ml of dry THF was added dropwise to 21.9 g (0.163 mol) of 1-chloro-3-methyl-3-phospholene (**3**) [10] in 140 ml of THF at 0°C with stirring under a nitrogen atmosphere. After the addition, the cooling bath was removed and the contents of the flask were stirred for 2 h. The

<sup>1</sup> 1-Bromo-2,4,6-tri-isopropylbenzene was prepared from 1,3,5-tri-isopropylbenzene by the procedure used for the bromination of 1,3-di-*tert*-butyl-5-methylbenzene [8]. Yield 78%; b.p. 85–90°C (0.15 mmHg) [lit. [9] 98–100°C (0.40 mmHg)].

solvent was evaporated and the residue extracted with 4 × 50 ml of n-hexane. The solvent of the combined extracts was evaporated to give 47.7 g (97%) of phosphine **4** (<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -37.1. MS *m/z* (rel. int.): 302 (M<sup>+</sup>, 100), 287 (77), 43 (80)).

The phosphine **4** obtained in the previous reaction was dissolved in 180 ml of chloroform and slowly treated with 20.8 g (0.183 mol) of 30% hydrogen peroxide at 0°C with intensive stirring. After a 1 h reaction time, the mixture was washed with 4 × 60 ml of water. The organic phase was dried (MgSO<sub>4</sub>) and the solvent evaporated to give 52.7 g (91%) of oxide **5**. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 60.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.07–1.35 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.82 (s, 3H, C<sub>3</sub>-Me), 2.70–3.55 (m, 7H, CH<sub>2</sub>, CH), 5.57 (d, <sup>3</sup>J(P,H) = 29.9, 1H, CH=), 7.05 (s, 2H, ArH). MS *m/z* (rel. int.): 318 (M<sup>+</sup>, 100), 303 (68), 43 (25). HRMS *M*<sub>found</sub><sup>+</sup> = 318.2081. C<sub>20</sub>H<sub>31</sub>OP. Calc.: 318.2113.

### 3.2. 3,4-Dibromo-3-methyl-1-(2,4,6-tri-isopropylphenyl)phospholane 1-oxide (**6**)

The solution of 2.5 ml (0.049 mol) bromine in 50 ml of chloroform was added dropwise to 15.5 g (0.049 mol) of phospholene oxide **3** in 100 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 solvent was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 19.6 g (84%) of **6** consisting of two diastereomers. <sup>31</sup>P NMR (CDCl<sub>3</sub>): 47.4 (81%) and 48.9 (19%). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for the major isomers: δ 30.3 (*J* = 3.8, C<sub>3</sub>-CH<sub>3</sub>), 42.8 (*J* = 60.9, C<sub>2</sub>), 49.0 (*J* = 61.2, C<sub>2</sub>), 57.4 (*J* = 6.6, C<sub>1</sub>), 66.7 (*J* = 8.3, C<sub>3</sub>); for the minor isomer: δ 31.7 (C<sub>3</sub>-CH<sub>3</sub>), 43.7 (*J* = 61.8, C<sub>2</sub>), 47.6 (*J* = 63.2, C<sub>2</sub>), 58.6 (*J* = 6.7, C<sub>1</sub>), 65.1 (*J* = 6.3, C<sub>3</sub>); common signals: δ 23.3 (C<sub>1</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 24.5 (C<sub>2</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 32.7 (*J* = 5.1, C<sub>2</sub>-CHMe<sub>2</sub>), 33.8 (C<sub>1</sub>-CHMe<sub>2</sub>), 122.2 (*J* = 11.6, C<sub>3</sub>), 151.5 (*J* = 11.7, C<sub>2</sub>), 152.7 (C<sub>1</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.22–1.37 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.92 (s, 0.57H, C<sub>3</sub>-Me for the minor isomer), 2.20 (s, 2.43H, C<sub>3</sub>-Me for the major isomer), 7.10 (s, 2H, ArH). MS *m/z* (rel. int.): 476 (M<sup>+</sup>, <0.5), 397 (55), 317 (100), 43 (38). CI-MS: 477 (M + H).

### 3.3. 3-Methyl-1-(2,4,6-tri-isopropylphenyl)phosphole (**2**)

The solution of 10.0 g (0.0209 mol) of dibromo compound **6** in 50 ml of dry benzene was added to the mixture of 5.6 ml (0.0690 mol) of pyridine, 2.3 ml (0.0230 mol) of trichlorosilane and 50 ml of benzene in a nitrogen atmosphere. After a period of 5 h of reflux, the insoluble materials were removed by filtration. The solvent of the filtrate was removed in vacuum and the crude product so obtained purified by column chro-

mography (silica gel, 3% methanol in chloroform) to afford 5.3 g (61%) of **2**; m.p. 70–72°C (acetone). <sup>31</sup>P NMR (CDCl<sub>3</sub>): -8.6. <sup>13</sup>C NMR, Table 1. <sup>1</sup>H NMR, Table 2. MS *m/z* (rel. int.): 300 (M<sup>+</sup>, 100), 285 (80), 189 (21), 43 (64). Anal. Found: C, 79.51; H, 9.30. C<sub>20</sub>H<sub>29</sub>P. Calc.: C, 79.94; H, 9.75%.

### 3.4. Dimer **10** of phosphole oxide **9**

The solution of 2.4 g (0.0080 mol) of phosphole **2** in 20 ml of chloroform was slowly treated with 1.02 g (0.0090 mol) of 30% hydrogen peroxide at 0°C with intensive stirring. After a 1 h reaction period, the mixture was washed with 3 × 10 ml of water. The organic phase was dried (MgSO<sub>4</sub>) and the solvent evaporated to give a crude product that was purified by column chromatography (silica gel, 3% methanol in chloroform). The yield of dimer **10** was 1.9 g (75%); m.p. 232–234°C (acetone/n-pentane 4:1). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 56.4 and 80.1 (*J*(P,P) = 38.1). <sup>13</sup>C NMR, Table 5. <sup>1</sup>H NMR, Table 7. MS, Table 8. Anal. Found: C, 75.61; H, 8.92. C<sub>40</sub>H<sub>58</sub>O<sub>2</sub>P<sub>2</sub>. Calc.: C, 75.92; H, 9.24%.

Oxidation of a small sample of phosphole **2** in CDCl<sub>3</sub> with one drop of 70% *tert*-butylperoxide at around 0°C resulted in the appearance of an intermediate signal for phosphole oxide **9** at δ = 49.2 ppm. Simultaneously with the disappearance of this signal, the shifts of the dimer **10** developed. After 1 h there was no **9** in the mixture.

### 3.5. *N*-Phenylmaleimide adduct **11** with phosphole oxide **9**

A mixture of 1.2 g (0.00251 mol) of dibromo compound **6**, 0.44 g (0.00254 mol) of *N*-phenylmaleimide,

Table 9  
Data for the X-ray analysis of phosphole **2**

Formula	C <sub>20</sub> H <sub>29</sub> P
Molecular weight	300.42
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
<i>a</i> (Å)	5.973(7)
<i>b</i> (Å)	23.065(9)
<i>c</i> (Å)	13.586(4)
<i>V</i> (Å <sup>3</sup> )	1861(2)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.072
<i>μ</i> (cm <sup>-1</sup> )	12.19
Min. transmission factor	0.96
Scan type	ω-2θ
Scan width (°)	(1.57 + 0.30 tg θ)
2θ <sub>max</sub> (°)	150.3
Measured reflections	4236
Unique reflections with <i>I</i> > 3σ( <i>I</i> )	3859
Final <i>R</i> and <i>R</i> <sub>w</sub> indices	0.079, 0.088
No. of variables	220
GOF	4.93

0.7 ml (0.00502 mol) of triethylamine and 25 ml of benzene was stirred at reflux for 8 h.

The precipitated salt was filtered off and the solvent of the filtrate evaporated. The crude product so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.9 g (73%) of **11**; m.p. 272–274°C (acetone). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 83.8. <sup>13</sup>C NMR, Table 6. <sup>1</sup>H NMR, Table 7. MS, Table 8. Anal. Found: C, 73.22; H, 7.08. C<sub>30</sub>H<sub>36</sub>NO<sub>3</sub>P Calc.: C, 73.60; H, 7.41%.

### 3.6. X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 9. A needle-shaped crystal of approximate dimensions 1.00 × 0.40 × 0.30 mm<sup>3</sup> was selected and mounted. Data were collected on a Rigaku AFC6S diffractometer, at -140.0°C, using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). The diffracted intensities were corrected for Lorentz, polarization and secondary extinction (coefficient 3.021 × 10<sup>-6</sup>). The structure was solved by direct methods and refined with full-matrix techniques. All non-hydrogen atoms were refined anisotropically. Hydrogens were generated based upon geometric evidence (C–H 0.95 Å). The final difference Fourier synthesis presented maximal residuals of 1.13 e<sup>-</sup> Å<sup>-3</sup> and -0.73 e<sup>-</sup> Å<sup>-3</sup>. The calculations were performed with the help of the teXsan package [11]. Full lists of atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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