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# New P-Ligands: The Aromaticity and Reactivity of 2,4,6-Trialkylphenylphospholes

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ABSTRACT: *A further member of 2,4,6-trialkylphenylphospholes, the ditertbutylmethylphenyl derivative (***1c***) was characterized by Bird index and by the sum of angles at the phosphorus atom to describe the flattening of the P-pyramid. Both numbers suggested a slight aromaticity. The reaction of arylphospholes with phosphorus tribromide was extended to phosphole* **1c** *leading this occasion, after further steps, to the mixture of 3- and 2-substituted products (***3c-1** *and* **3c-2**, *respectively). A triisopropylphenyl-2H-phosphole (***4***) formed by sigmatropic rearrangement was utilized in the preparation of new 1-phosphanorbornene derivatives, such as sulfide* **6** *and hemi-oxides* **8-1** *and* **8-2**. *Further oxidation of the latter species (***8-1** *and* **8-2***) led to the decomposition of the dimeric structure (***11***). **4** could also be trapped by benzaldehyde to afford the oxaphosphanorbornene (***10***) as one diastereomer. Finally, the reversible formation of 2H-phosphole* **4** *from 1H-phosphole* **1a** *at 150°C was proved.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:104–110, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20077

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## *INTRODUCTION*

2,4,6-Trialkylphenylphospholes introduced recently by Quin and one (GK) of the above authors [1–3] form a special group of phospholes, perhaps the most important simple P-heterocycles that are widely used as P-ligands [4,5]. While in the "common or garden variety" of phospholes there cannot be electron delocalization due to the pyramidal geometry around the phosphorus atom [6], the phospholes with sterically demanding substituent on the phosphorus atom may be of certain aromaticity due to the flattening of the P-pyramid [7].

The synthesis, properties, and reactivity of 2,4,6-trialkylphenylphospholes were described in earlier publications [1–3, 7–12]. In this paper, the recent findings of ours on the physical and chemical properties of trialkylphenylphospholes are discussed.

So far the 2,4,6-triisopropylphenyl- and the tri*tert*butylphenylphospholes (**1a** and **1b**) have been characterized by Bird indexes (BI) [13] of 40.4 [2] and 56.5 [3], respectively, based on the bond equalizing in the hetero ring. For arylphospholes **1a** and **1b**,

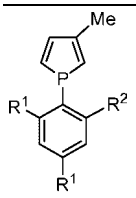
the sum of the angles at the phosphorus atom, introduced by Schmidpeter as the measure of flattening [14], was found to be 314.4 [2] and 331.7 [3], respectively. For phospholes with pyramidal geometry at P, this number is around 302 [15]. The indicators of **1b** suggested an aromaticity that is comparable with that of pyrrole (BI = 59).

## *RESULTS AND DISCUSSION*

We could obtain the 2,4-di*tert*butyl-6-methylphenylphosphole (**1c**) [1] in a crystalline form suitable for X-ray analysis. The perspective view of arylphosphole **1c** together with some bond lengths and bond angles are shown in Fig. 1. The flattening of the P-pyramid in **1c** allowing some extent of electron delocalization can be characterized by a BI of 42.3 that is comparable with that of **1a** and suggests a moderate aromaticity. The sum of angles around P was found to be 317.0 for **1c** similar to that found for **1a** that is again in agreement with a slight degree of aromaticity. The factors characterizing the aromaticity of phospholes **1a–c** are summarized in Table 1.

A significant difference was found between the reactivity of arylphospholes **1b** and **1a** toward phosphorus tribromide. The interaction of **1b** with phosphorus tribromide led to 3-substitution; reaction of the dibromophosphanylphosphole intermediate so obtained with morpholine gave phosphonous amide **2b-1**, and after oxidation phosphonic amide **3b-1** (Scheme 1). At the same time, a similar sequence of reaction of **1a** resulted in 2-substituted products **2a-2** and **3a-2** (Scheme 1). The selectivity of these reactions was explained by steric factors [10]. It was now observed that the interaction of **1c** with phosphorus tribromide followed by treatment of the intermediate with morpholine furnished a ca 6:4 mixture of both possible phosphonous amides **2c-1** and **2c-2**, or after oxidation phosphonic amides **3c-1** and **3c-2** (Scheme 1).

**TABLE 1** Factors Characterizing the Planarization of the P-Pyramid in Trialkylphenylphospholes **1a–c**




**1**

| | $R^1$ | $R^2$ | BI [13] | Sum of Angles at P [14] | Ref. |
|---|---|---|---|---|---|
| **1a** | *i*-Pr | *i*-Pr | 40.4 | 314.4 | [2] |
| **1b** | *t*-Bu | *t*-Bu | 56.5 | 331.7 | [3] |
| **1c** | *t*-Bu | Me | 42.3 | 317.0 | |

Contrary to the transformations of **1a** and **1b** [10], that of **1c** was not so clear-cut. Still, the outcome is interesting and confirms our earlier explanation regarding the importance of steric factors. The di*tert*butyltolyl substituent occupies clearly an intermediate position between the triisopropylphenyl and the supermesityl ones regarding the steric hindrance caused by the orthoalkyl substituents. Products **3c-1** and **3c-2** of the relatively complex reaction mixture were identified by $^{31}$P NMR data including stereospecific $J_{PP}$ couplings and by HR-FAB data. Comparison of the $^{31}$P NMR data of the isomers of **3c** with those of the earlier described products **3b-1** and **3a-2**, which were prepared in pure form and characterized fully [10], is shown in Table 2.

It was observed by us that the slightly aromatic triisopropylphenyl- and the di*tert*butyltolyl-1*H*-phospholes (**1a** and **1c**) underwent a sigmatropic rearrangement at 150°C to afford the corresponding

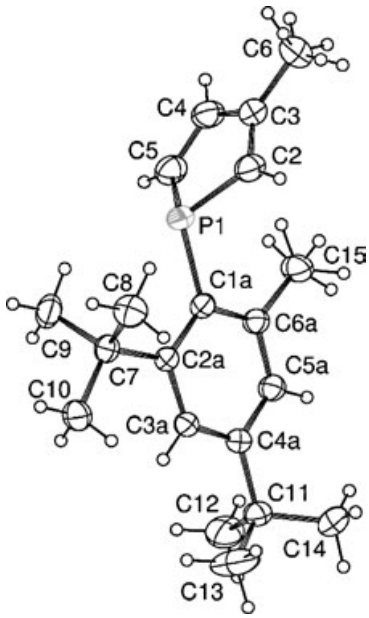
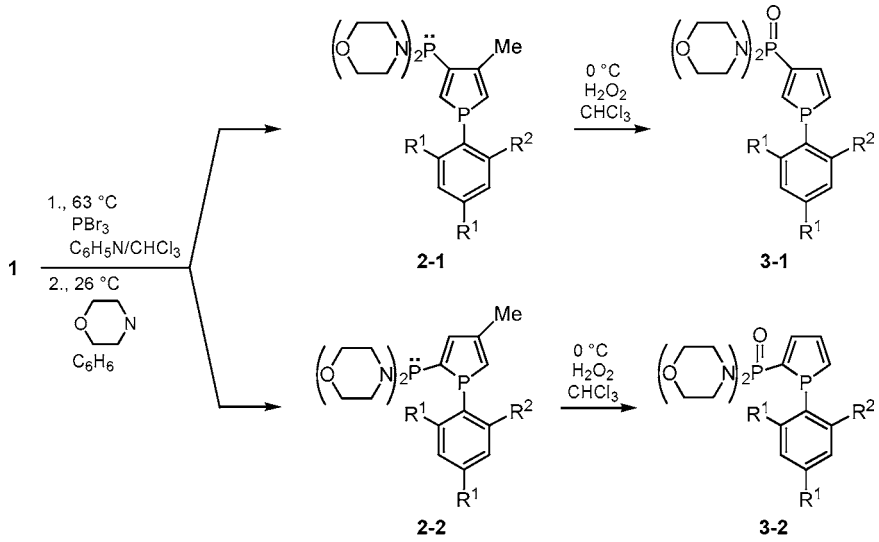



**FIGURE 1** The ortep diagram of **1c** (the ellipsoid probability is 30%) with the geometrical data selected P(1)–C(2) 1.768(4), C(2)–C(3) 1.343(5), C(3)–C(4) 1.426 (5), C(4)–C(5) 1.333(5), C(5)–P(1) 1.761 (4), C(3)–C(6) 1.502(5), P(1)–C(1A) 1.839(3); C(5)–P(1)-C(2) 91.04(17), C(5)–P(1)-C(1a) 112.21(15), C(2)–P(1)-C(1a) 113.83(14). C(6) and C(15) methyl hydrogen atoms are in disordered positions.

**TABLE 2** $^{31}$P NMR Shifts $\delta$ and Coupling Constant **J** (Hz) of **3-1** and **3-2** ($CDCl_3$)

| | 3–1 | | | 3–2 | | | |
|---|---|---|---|---|---|---|---|
| | $\delta$ | $\delta$ | $^3J_{pp}$ | $\delta$ | $\delta$ | $^2J_{pp}$ | Ref. |
| **b** | 7.1 | 23.4 | 21.8 | | | | [10] |
| **a** | | | | 0.9 | 24.1 | 49.4 | [10] |
| **c** | 4.2 | 22.2 | 15.9 | 10.5 | 23.4 | 45.4 | |




| | $R^1$ | $R^2$ | 3-1* | 3-2* | Ref. |
|---|---|---|---|---|---|
| **b** | *t*-Bu | *t*-Bu | 100 | – | [3] |
| **a** | *i*-Pr | *i*-Pr | – | 100 | [2] |
| **c** | *t*-Bu | Me | 57 | 43 | |

*Product composition [%] on the basis of $^{31}$P NMR intensities

**SCHEME 1**

2*H*-phospholes (e.g. **4**) that were trapped by diphenylacetylene to yield an aryl-1-phosphanorbornadiene (e.g. **5**). Intermediate **4** also dimerizes leading to the isomers of 1,2-diphosphanorbornene derivative **7** (Scheme 2) [12].

Trapped product **5** has now been identified as its P-sulfide (**6**), and the isomers of dimer **7** have been converted to monoxides **8-1** and **8-2** (Scheme 2). Products **6**, **8-1**, and **8-2** were characterized by $^{31}$P, $^{13}$C, and $^{1}$H NMR, as well as HR-FAB data.

Monoxides **8-1** and **8-2** could only be obtained under controlled conditions involving 0°C, intensive stirring and only a slight excess of the hydrogen peroxide. Using more of the oxidizing agent and allowing the temperature to reach 26°C, a complex mixture was obtained with phosphole oxide dimer **12** as the main component [12]. Formation of 7-phosphanorbornene **12** can be explained by assuming that the bis(phosphine oxide) **11** is not stable and hence is decomposed to the corresponding phosphole oxide that is dimerized instantly (Scheme 3).

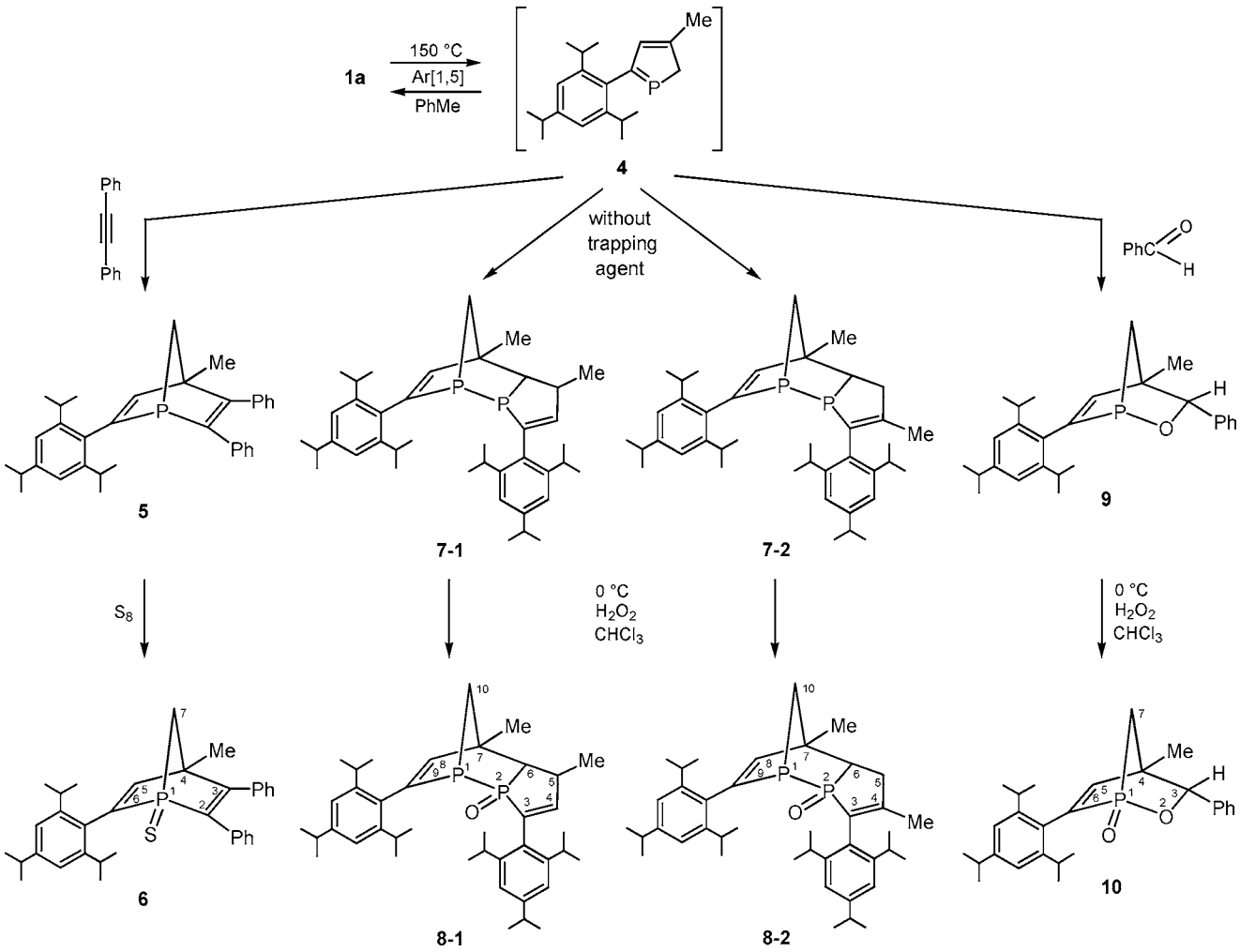
We wished to test if 2*H*-phosphole intermediate **4** can also be trapped by benzaldehyde. Heating the toluene solution of phosphole **1c** and benzaldehyde to 150°C in a sealed tube for 2 weeks led to the formation of oxaphosphanorbornene **9** that was converted to the more stable phosphinate form (**10**) (Scheme 2).

Product **10** was identified by $^{31}$P, $^{13}$C, and $^{1}$H NMR data, as well as HR-FAB. Due to the instability of cyclic phosphinate **10**, only a small layer of silica gel was used during the column chromatography.

It is noteworthy that in the analogous reaction of the Mathey phosphole (that is the 3,4-dimethyl-1-phenylphosphole), the corresponding phosphinate was obtained as a 82:18 mixture of endo and exo fused isomers [16]. In our case, the cycloaddition seemed to be stereoselective affording only one isomer of **9** (after oxidation **10**) that was presumably the endo cycloadduct.

Finally, the 2*H*-phosphole (**4**) generated at 150°C was attempted to be trapped by *N*-phenylmaleimide (NPMI). **1a** did not react, however, in the 2H-phosphole (**4**) form, but as a 1*H*-phosphole to afford 7-phosphanorbornene **13** that was, surprisingly, the exo fused isomer. Oxidation of phosphine **13** led to phosphine oxide **14** formed by inversion of the P-centrum (Scheme 4).

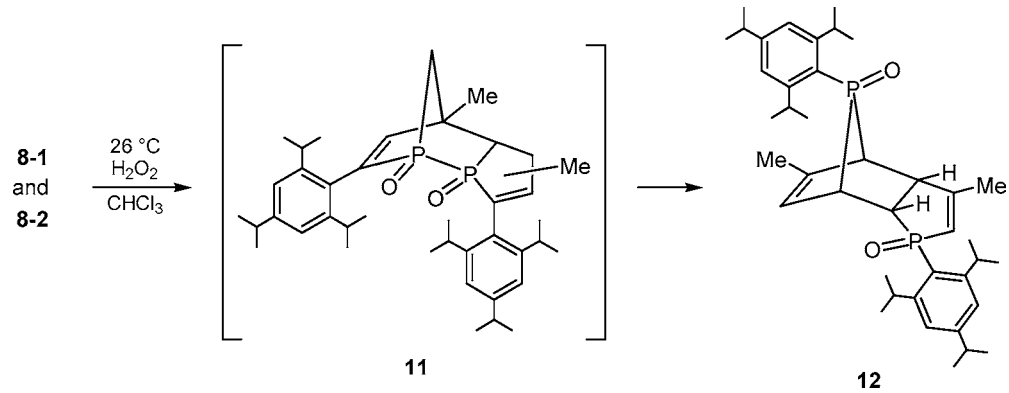
The formation of cycloadduct **13** was not efficient in itself, still proves that at 150°C there is an equilibrium between the 1*H*- and the 2*H*-phosphole forms as was suggested [17] and as is shown in Scheme 2. It is also seen that the NPMI may react only with the 1*H*-phosphole component of the equilibrium. Spectral parameters of phosphine **13** and phosphine oxide **14** were identical



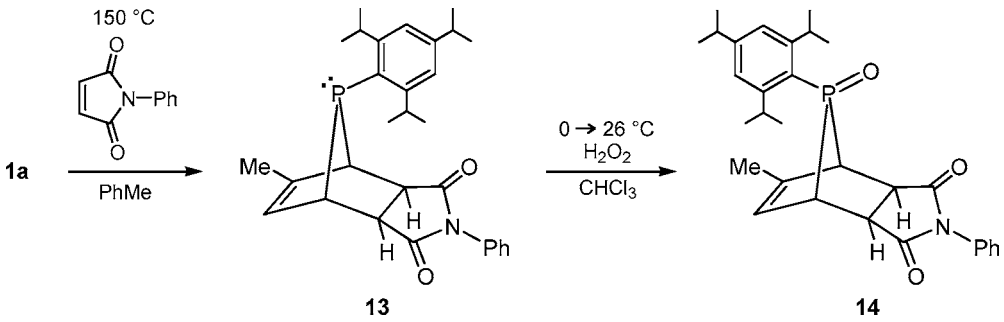

SCHEME 2

with those of authentic samples deriving from the Diels Alder reaction of **1a** and NPMI carried out at 110°C [11] (see Experimental). It was surprising, however, that not even traces of the endo fused isomer could be pointed out in the reaction realized at 150°C.

It was also interesting to find that at 110°C, aryl-1*H*-phosphole **1a** did not enter into reaction with




SCHEME 3




SCHEME 4

diphenylacetylene indicating that this dienophile can react only with a 2*H*-phosphole.

To summarize our results, the geometrical data obtained by X-ray made possible to characterize the flattening of the P-pyramid in di*tert*butyltolylphosphole. The reaction of arylphospholes with phosphorus tribromide was extended to di*tert*butyltolylphosphole that, in contrast to earlier cases, was not substituted in a site-selective manner. Sigmatropic rearrangement of the triisopropylphenylphosphole made available the preparation of new products, such as a 1-phosphanorbornadiene sulfide and the hemi-oxide of the dimer that may be an intermediate on way of the decomposition of the dimer. The use of benzaldehyde as trapping agent led to an oxaphosphanorbornene in a selective reaction. The result of the reaction of one arylphosphole with NPMI at 150°C proved the equilibrium between the corresponding 1*H*-phosphole and 2*H*-phosphole. Utilization of the new P-ligands in transition metal complexes and the test of these complexes as catalysts is a further challenge for us.

## *EXPERIMENTAL SECTION*

The $^{31}P$, $^{13}C$, and $^{1}H$ NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% $H_3PO_4$ or TMS. The couplings are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

The arylphospholes **1a** and **1c** were prepared as described earlier [1,2].

### *Single Crystal X-ray Analysis of 1-(2,4-Ditert-butyl-6-methylphenyl-)3-methylphosphole (**1c**)*

A colorless needle crystal of **1c** was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu $K_\alpha$ radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 15 carefully centered reflections in the range $20.03 < 2\theta < 26.24°$. The data were collected using the $\omega$-$2\theta$ scan technique to a maximum $2\theta$ value of 151.2°. Of the 8612 reflections, which were collected, 3787 were unique ($R_{int} = 0.084$). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Data processing was carried out using the software supplied with the diffractometer. The structure was solved by direct methods [18] and expanded using Fourier techniques [19]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated based upon geometric evidence and their positions were refined by the riding model. All calculations were performed using the teXsan [20] crystallographic software package of Molecular Structure Corporation except for refinement, which was performed using SHELXL-97 [21] with full matrix least squares method on $F^2$. The details are shown in Table 3. CCDC 252411 contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk).

### *The Reaction of 1-(2,4-Ditertbutyl-6-methylphenyl-)3-methylphosphole (**1c**) with Phosphorus Tribromide Followed by Functionalization of the Intermediate*

0.12 mL (1.26 mmol) of phosphorus tribromide and 0.10 mL (1.24 mmol) of pyridine were added to 0.35 g (1.17 mmol) of **1c** in 50 mL of dry $CHCl_3$, and the solution was stirred at the boiling point for 48 h in

**TABLE 3** Crystal Data and Structure Refinement for **1c**

| | |
|---|---|
| Empirical formula | $C_{20}H_{29}P$ |
| Formula weight | 300.40 |
| Temperature | 293(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | $a = 6.079(8)$ Å |
| | $b = 17.25(2)$ Å $\beta = 93.47(4)^\circ$ |
| | $c = 17.769(4)$ Å |
| Volume | 1860(3) Å$^3$ |
| $Z$ | 4 |
| Density (calculated) | 1.073 g cm$^{-3}$ |
| Absorption coefficient | 1.225 mm$^{-1}$ |
| $F(000)$ | 656 |
| Crystal size | 0.75 × 0.40 × 0.25 mm$^3$ |
| Theta range for data collection | 3.57–75.62° |
| Index ranges | $-7 \le h \le 7$, $-21 \le k \le 21$, $-22 \le l \le 22$ |
| Reflections collected | 8318 |
| Independent reflections | 3787 [$R$(int) = 0.0836] |
| Completeness to theta = 75.62° | 97.9% |
| Absorption correction | PSI |
| Max. and min. transmission | 0.995 and 0.879 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data/restraints/parameters | 3787/0/190 |
| Goodness-of-fit on F$^2$ | 1.032 |
| Final $R$ indices [$I > 2$sigma($I$)] | $R_1 = 0.0578$, $wR_2 = 0.1371$ |
| $R$ indices (all data) | $R_1 = 0.1228$, $wR_2 = 0.1666$ |
| Largest diff. peak and hole | 0.209 and −0.270 e Å$^{-3}$ |

the nitrogen atmosphere. The volatile components were removed in vacuo to give a mixture of the corresponding bromo-intermediates.

The mixture of the bromo-intermediates so obtained was taken up in dry benzene (50 mL) and treated with morpholine (0.35 mL, 4.0 mmol) at 0°C. After stirring at room temperature for 1 h, the mixture was filtered and the solvent of the filtrate was evaporated to afford a 6:4 mixture of phosphonous amides **2-1** and **2-2**.

The bisphosphines **2** so obtained were dissolved in $CHCl_3$ (50 mL) and oxidized by the addition of 0.68 mL (∼6.0 mmol) of 30% hydrogen peroxide at 0°C. After stirring at room temperature for 1 h, the mixture was extracted with 2 × 20 mL of water. The organic phase was dried ($Na_2SO_4$), the solvent evaporated, and the residue so obtained purified by repeated column chromatography (silica gel, 3% MeOH in $CHCl_3$) to furnish a 57:43 mixture of **3c-1** and **3c-2**.

$^{31}$P NMR data can be found in Table 2. $(M+H)^+_{found} = 519.2870$, $C_{28}H_{45}N_2O_3P_2$ requires 519.2905.

### *Synthesis of 4-Methyl-2,3-diphenyl-6-(2,4,6-triisopropylphenyl-)1-phosphanorborna-2,5-diene 1-sulfide (**6**)*

Phosphole **1a** was reacted with tolane at 150°C as described earlier to give cycloadduct **4** [12]. 0.48 g (1.0 mmol) of **4** and 0.10 g (3.0 mmol) of sulfur in 50 mL of degassed benzene was heated at the boiling point in the nitrogen atmosphere for 20 h. Solvent was evaporated and the residue purified by column chromatography (silica gel, benzene–acetone 4:6) to give 0.36 g (67%) of **6**.

$^{31}$P NMR ($CDCl_3$) $\delta$ 58.9; $^{13}$C NMR ($CDCl_3$) $\delta$ 21.3 ($J$ = 14.4, $C_4$–Me), 23.1 ($CH_3CH$), 24.0 ($CH_3CH$), 24.2 ($2CH_3CH$), 24.9 ($CH_3CH$), 25.4 ($CH_3CH$), 31.5 ($o$-$CHMe_2$), 34.3 ($p$-$CHMe_2$), 53.1 ($J$ = 20.5, $C_4$), 73.4 ($J$ = 57.5, $C_7$), 141.5 ($J$ = 56.1, $C_2$), 146.4 ($J$ = 3.0, $C_{2'}$),* 147.2 ($J$ = 3.6, $C_{6'}$), *148.4 ($C_{4'}$), 150.5 ($J$ = 53.6, $C_6$), 152.5 ($J$ = 14.5, $C_5$), 161.4 ($J$ = 13.4, $C_3$), *may be reversed; $^1$H NMR ($CDCl_3$) $\delta$ 0.89 (d, $J$ = 6.8, 3H, $CHCH_3$), 1.14 (d, $J$ = 6.7, $CHCH_3$), 1.31 (d, $J$ = 6.9, $CHCH_3$), 1.36 (d, $J$ = 6.8, $2CHCH_3$), 1.47 (d, $J$ = 6.8, $CHCH_3$), 1.57 (s, 3H, $C_4$–$CH_3$), 2.60 (q, $J$ = 6.8, 1H, $CHMe_2$), 2.95–3.09 (m, 3H, $CHMe_2$, $CH_2$), 3.27 (q, $J$ = 6.8, 1H, $CHMe_2$), 7.11 (d, $J$ = 7.1, CH = overlapped by the aromatic signals); HR-FAB, $(M+H)^+_{found} = 511.2521$, $C_{34}H_{40}PS$ requires 511.2588.

### *Synthesis of the Monoxide of the Dimer of 3-Methyl-5-(2,4,6-triisopropylphenyl-)2H-phosphole (**8**)*

Phosphole **1a** was converted to the isomers of dimer **7** as described earlier [12]. 0.40 g (0.67 mmol) of **7** in 40 mL of chloroform was treated with 0.12 mL (∼1.01 mmol) of 30% hydrogen peroxide at 0°C on intensive stirring. After 2 h the mixture was extracted with 3 × 10 mL of water. The organic phase was dried ($Na_2SO_4$) and the solvent evaporated. The crude product was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.20 g (48%) of **8** as a mixture of a major (**8-1**, 77%) and a minor (**8-2**, 23%) isomer. M+H = 617; $(M+H)^+_{found}$ = 617.3951, a $C_{40}H_{59}OP_2$ requires 617.4041.

**8-1**: $^{31}$P NMR ($CDCl_3$) $\delta$ −40.1 and 113.0, ($^1J_{PP} = 219.8$); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.2 ($J$ = 8.0, $C_5$–Me)[a], 22.8 ($CHCH_3$), 23.1 ($J$ = 6.9, $C_7$–Me)[a], 23.4 ($CHCH_3$), 27.3 ($CHCH_3$), 23.8 ($CHCH_3$), 23.9 ($4CHCH_3$), 24.8 ($CHCH_3$), 25.5 ($CHCH_3$), 25.8 ($CHCH_3$), 27.0 ($CHCH_3$), 29.5 ($o$-$CHMe_2$), 30.9 ($o$-$CHMe_2$), 31.5 ($o$-$CHMe_2$), 31.7 ($o$-$CHMe_2$), 34.1 ($p$-$CHMe_2$), 34.2 ($p$-$CHMe_2$), 39.3 ($J$ = 12.9, $C_7$), 44.8 ($J_1$ = 15.8, $J_2$ = 11.2, $C_{10}$), 47.6 ($J$ = 58.5, $C_6$), 59.0 ($J_1$ = 9.3, $J_2$ = 6.9, $C_7$), 120.1 ($C_{3'}$, $C_{3''}$)[b], 121.0 ($C_{5'}$)[b], 121.3 ($C_{5''}$)[b], 127.3 ($J$ = 7.2, $C_{1'}$), 130.0 ($J$ = 14.9, $C_9$),

138.0 ($J_1 = 61.0$, $J_2 = 10.4$, $C_3$), 140.0 ($J = 7.8$, $C_{1''}$), 145.5 ($J = 2.9$, CPr)[c], 146.7 (2CPr)[c], 147.5 (CPr)[c], 147.8 (CPr)[c], 148.0 (CPr)[c], 150.9 ($J = 9.2$, $C_8$), 151.4 ($J = 29.2$, $C_4$).

**8-2**: $^{31}$P NMR ($CDCl_3$) $\delta$ −40.8 and 116.1, ($J_{PP}$ = 215.9); $^{13}$C NMR ($CDCl_3$) $\delta$ 22.4 ($J = 7.8$, $C_5$–Me)[d], 22.8 (CH*C*H$_3$), 24.1 ($J = 10.0$, $C_7$–Me)[d], 36.3 ($J$ = 13.3, $C_5$), 38.3 ($J = 60.9$, $C_6$), 44.1 ($J_1 = 16.0$, $J_2$ = 11.0, $C_{10}$), 58.8 ($J_1 \sim J_2 \sim 8.0$, $C_7$), 126.2 ($J = 7.0$, $C_{1'}$), 129.9 ($J = 15.0$, $C_9$), 138.0 ($J_1 = 61.0$, $J_2$ =10.4, $C_3$), 139.8 ($J = 8.0$, $C_{1''}$), 145.9 (CPr)[e], 146.8 (CPr)[e], 147.5 (CPr)[e], 147.7 (CPr)[e], 148.3 (CPr)[e], 150.7 ($J = 9.1$, $C_8$), 156.1 ($J = 29.0$, $C_4$). [a–e] tentative assignment.

### *Synthesis of 4-Methyl-3-phenyl-6-(2,4,6-triisopropylphenyl-)2,1-oxaphosphanorborn-5-ene 1-oxide (**10**)*

A mixture of 0.50 g (1.7 mmol) of **1a** and 0.51 mL (5.0 mmol) of benzaldehyde in 15 mL of toluene was degassed by nitrogen and heated in a sealed tube at 150°C for 2 weeks. The solvent was evaporated to yield 0.68 g (∼100%) of **9** ($^{31}$P NMR ($CDCl_3$) $\delta$ 118.3; $(M+H)^+_{found}$ = 407.2428, $C_{27}H_{36}OP$ requires 407.2504).

Phosphinous ester **9** (0.68 g, ∼1.7 mmol) in 30 mL of chloroform was treated with 0.58 mL (∼5.1 mmol) of 30% hydrogen peroxide on stirring at 0°C. After 1.5 h the mixture was extracted with 2 × 10 mL of water and the organic phase was dried ($Na_2SO_4$). The crude product obtained after evaporating the solvent was purified by flash column chromatography (using a 1 cm silica gel layer and 1% methanol in chloroform eluant) to furnish 0.32 g (42%) of **10** in a purity of ∼95%.

$^{31}$P NMR ($CDCl_3$) $\delta$ 58.6; $^{13}$C NMR $\delta$ 19.9 ($J$ = 16.8, $C_4$–Me), 22.9 (CH*C*H$_3$), 23.5 (CH*C*H$_3$), 24.0 (CH*C*H$_3$), 31.0 ($CHMe_2$), 31.1 ($CHMe_2$), 33.3 ($CHMe_2$), 38.4 ($J$ = 86.8, $C_7$), 45.0 ($J$ = 24.0, $C_4$), 83.9 ($C_3$), 141.0 ($J$ = 101.2, $C_6$), 152.3 ($J$ = 19.3, $C_5$); HRFAB, $(M+H)^+_{found}$ = 423.2369, a $C_{27}H_{35}O_2P$ requires 423.2453.

### *The reaction of **1a** with N-Phenylmaleimide at 150°C*

The reaction of 0.20 g (0.67 mmol) of **1a** and 0.12 g (0.70 mmol) of NPMI was carried out similarly as the **1a** → **9** transformation with a reaction time of 3 days to afford cycloadduct **13** in ca 33% conversion. $^{31}$P NMR ($CDCl_3$) $\delta$ 2.1 ($\delta_P$ lit [11] 2.1); FAB-MS, 473 (M+H).

Oxidation of the crude mixture by 30% hydrogen peroxide (as above) led to **14**. $^{31}$P NMR ($CDCl_3$) $\delta$ 85.7 ($\delta_P$ lit [11] 85.6); FAB-MS, 489 (M+H).

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