The effect of a sterically demanding P-substituent on the reactivity of P-heterocycles: selective transformations during the ring enlargement of a 1-(2,4,6-triisopropylphenyl)-2,5-dihydro-1*H*-phosphole 1-oxide †

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Dichlorocyclopropanation of the title dihydrophosphole oxide (**5**) by $CHCl_3$–$NaOH/H_2O$ under phase transfer catalysis (PTC) gave adduct **6A** in a selectivity of 80%. The use of sodium trichloroacetate as the precursor of dichlorocarbene resulted in, however, the exclusive formation of the other isomer (**6B**) exhibiting the same stereostructure, as the product formed in the liquid–liquid two-phase dichlorocyclopropanation of the phenyl-dihydrophosphole (**1**). The base- and thermo-induced cyclopropane ring opening of the adducts (**6A** and **6B**) led, surprisingly, to distinct dihydrophosphinine isomers (**7** and **8**, respectively) in a fully selective manner. The unusual reactivity of the P-heterocycles (**5** and **6**) is due to the sterically demanding *P*-aryl substituent. Semiempirical calculations on the *P*-aryl dihydrophosphinines (**7** and **8**) revealed a geometry and electron distribution that explains the unique NMR features observed.

Introduction

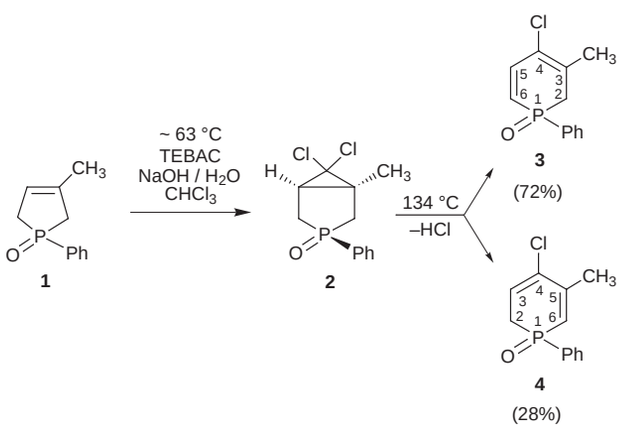
The ring enlargement of 5- and 6-membered P-heterocycles is a useful method for the synthesis of 6- and 7-membered ring products.[1,2] The simplest way to achieve ring expansion involves the addition of a dichlorocarbene unit to the double-bond of the starting P-heterocycle followed by the opening of the dichlorocyclopropane ring thus formed. In this way, a variety of 2,5-dihydro-1*H*-phosphole oxides were transformed to 1,2-dihydrophosphinine oxides[3–6] and to 1,2,3,6-tetrahydrophosphinine oxides,[6,7] while the dihydro- and tetrahydrophosphinines were converted to phosphepine derivatives.[8,9] It is known that the attachment of a sterically demanding group to the phosphorus atom may have an impact on the stability, geometry and chemical behaviour of the molecule.[10] As a part of our project on the synthesis of P-heterocycles with various kinds of sterically demanding protecting groups, we wished to prepare some *P*-(2,4,6-trialkylphenyl)dihydrophosphinine oxides that can be the starting materials for phosphabicyclo[2.2.2]octane derivatives, potential precursors of low-coordinated P-fragments.[11] In this paper, the synthesis of 1-(2,4,6-triisopropylphenyl)-1,2-dihydrophosphinine oxides and the intermediates leading to them is described.

† Representations of the electrostatic potential maps of the van der Waals surfaces of compounds **4** and **7** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/1999/1801, otherwise available from BLDSC (SUPPL. NO. 57554, pp. 2, 1999) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

Results and discussion

1. Ring enlargement of 1-(2,4,6-triisopropylphenyl)-3-methyl-2,5-dihydro-1*H*-phosphole 1-oxide (5)

In our earlier work, *P*-phenyl dihydrophosphole oxide **1** was reacted with dichlorocarbene generated from chloroform by aqueous sodium hydroxide under PTC conditions to give the phosphabicyclo[3.1.0]hexane as a single isomer **2** (Scheme 1).[3,12]



Scheme 1 (ref. 3, 4, 12)

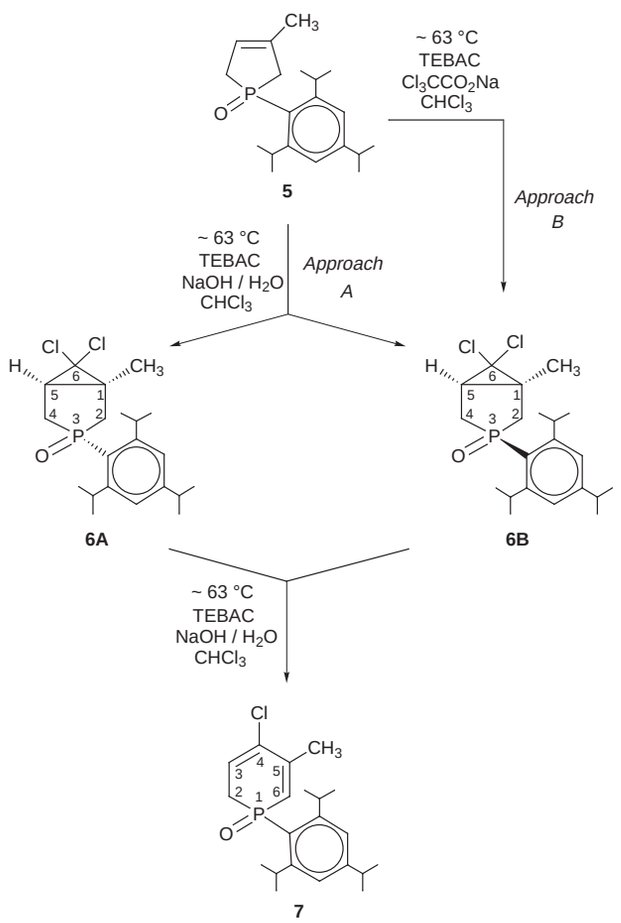
The 1-(2,4,6-triisopropylphenyl)-dihydrophosphole oxide (**5**), available from previous work[13] was reacted in a similar way. However, in accord with the enhanced reactivity of the double-bond, the dichlorocarbene was used in a smaller excess. The

Table 1 ^{31}P and ^{13}C NMR data for phosphabicyclohexane oxides **6A** and **6B** in $CDCl_3$ solution

Compound	δ_P	δ_C ($J_{P,C}$ in Hz) C_1	C_2	C_4	C_5	C_6	C_1-CH_3	$C_{1'}$ [a]	$C_{2'}$ [a]	$C_{3'}$ [a]	$C_{4'}$ [a]	*ortho*-$CHMe_2$	*para*-$CHMe_2$	$C_{2'}$-$CH(CH_3)_2$	$C_{4'}$-$CH(CH_3)_2$
6A	80.6	37.1 (8.0)	40.2 (63.4)	35.3 (64.7)	38.3 (6.5)	71.6 (5.8)	21.9 (8.2)	126.3 (86.9)	153.4 (11.4)	123.1 (11.0)	152.6 (2.0)	31.2 (3.6)	34.1	24.8,[b] 25.4[c]	23.7[b,c]
6B	77.9	36.2 (8.9)	41.0 (66.9)	34.9 (67.5)	36.7 (7.4)	72.8 (16.6)	21.6 (4.7)	127.2 (91.5)	151.9 (11.1)	122.5 (10.7)	152.5	32.7 (4.6)	34.1	25.0,[d] 25.1[e]	23.6[d,e]

[a] Carbon atom of the aromatic ring. [b–e] Tentative assignment.

reaction afforded the adduct with dichlorocarbene as a 4:1 mixture of isomers **6A** and **6B** (Scheme 2, *Approach A*). The



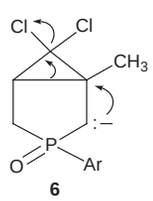
Scheme 2

isomeric composition of the phosphabicyclohexane (**6**) may be explained by the steric hindrance due to the space demanding *P*-aryl substituent: the diastereomer where the dichlorocyclopropane ring and the *P*-aryl group are in the *trans* disposition (**6A**) may be more easily formed than the other one with *cis* geometry (**6B**). As was shown above, this latter type of phosphabicyclohexane (**2**), where the electronic interaction between the lone electron pairs of the oxygen atom and the *endo* chlorine is minimal, was the result of the dichlorocyclopropanation of the *P*-phenyl dihydrophosphole oxide (**1**).[3,12]

Interestingly, the reaction of dihydrophosphole **5** with dichlorocarbene generated from sodium trichloroacetate under PTC conditions, gave isomer **6B** exclusively (Scheme 2, *Approach B*). The reason for the selectivity is not yet clear.

The structures of the phosphabicyclohexanes (**6A** and **6B**) were confirmed by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectroscopical methods. The ^{31}P and ^{13}C NMR spectral parameters are listed in Table 1. The chemical shifts and couplings were similar to those reported for other phosphabicyclohexanes.[3,5,12] The stereospecific ^{3}J(P,C) couplings observed on C_6 of the isomers of product **6** are in accord with the assignment suggested above. Thus, on the basis of earlier studies,[13] the ^{3}J(P,C) of 16.6 Hz detected on C_6 of **6B** seems to be consistent with the *cis* disposition of the *P*-aryl group and the dichlorocyclopropane ring, while the corresponding coupling of 5.8 Hz observed in **6A** may justify assignment of the *trans* geometry. For the P–Ph phosphabicyclohexane (**2**), whose stereostructure was confirmed by single crystal X-ray analysis,[12] a ^{3}J(P,C) of 14.4 Hz was reported.[13] The P-NMR chemical shifts of 80.6 and 77.9 ppm observed for **6A** and **6B**, respectively, are also consistent with the above stereochemical assignment. Earlier data show that the isomer with the *trans* geometry has the more downfield shift.[12,14] The methyl groups of the *ortho* isopropyl substituent in compounds **6A** and **6B** were doubled in the ^{13}C-NMR spectra due to the diastereotopy.

We observed that during the dichlorocyclopropanation of dihydrophosphole **5** according to "*Approach A*", a considerable proportion (*ca.* 48%) of dihydrophosphinine oxide **7** was also formed beside the phosphabicyclohexanes **(6A** and **6B)**



6

(Scheme 2). Dihydrophosphinine **7** was probably formed from the isomers of **6** by base-induced opening of the dichlorocyclopropane ring. This seems to be confirmed by the observation that the **7**:**6** proportion increased with the increase in the quantity of the sodium hydroxide used. In the course of the preparation of the phosphabicyclohexanes, we have never been able to observe the base-induced opening of the cyclopropane ring.[3,5,6] It is also noteworthy that the dihydrophosphinine oxide was formed as a single isomer (**7**) in a selective manner; in earlier syntheses, the dihydrophosphinines were always formed as the mixture of two double-bond isomers.[4–7] The dihydrophosphinine (**7**) revealed an anomalous ^{31}P NMR shift of 45.9; for the phenyl derivative a δ_P of 14.2 was detected.[7] The ^{1}H NMR data were decisive in proving isomeric structure **7**; it was clear that the olefinic protons are not vicinal. It is worth mentioning that contrary to the case of the *P*-phenyl dihydrophosphinine (**4**),[7] the C_3-H of **7** is not coupled by the phosphorus atom, or by the protons of the adjacent CH_2 group. The ^{13}C NMR spectral parameters of **7** also show some peculiarities compared to those of the *P*-phenyl derivative (**4**),[7] but nevertheless are in agreement with structure **7** (Table 2). The downfield shift of 129.9 ppm for C_6 and the coupling of 16 Hz observed on C_5 for structure **7** are particularly worthy of a mention. These anomalous effects may be due to the special geometry of aryldihydrophosphinine **7** that is the consequence of the presence of the sterically demanding P-substituent (see next section). The assignments were supported by a spectrum obtained by the attached proton test (APT) technique. The ^{1}H and ^{13}C NMR assignments were confirmed by two dimensional correlation

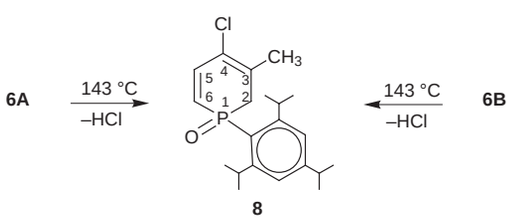
Table 2 ^{31}P and ^{13}C NMR data for dihydrophosphinine oxides **3**, **4**, **7** and **8**

Compound	δ_P	δ_C ($J_{P,C}$ in Hz) C_2	C_3	C_4	C_5	C_6	=C-CH_3	$C_{1'}$ [a]	$C_{2'}$ [a]	$C_{3'}$ [a]	$C_{4'}$ [a]	*ortho*-$CHMe_2$	*para*-$CHMe_2$	$C_{2'}$-$CH(CH_3)_2$	$C_{4'}$-$CH(CH_3)_2$
7	45.9	35.8 (73.3)	117.8 (14.7)	140.2 (15.6)	153.5 (16.0)	129.9 (92.7)	16.5 (16.9)	126.6 (106.1)	151.7 (11.3)	122.5 (11.5)	152.4 (2.1)	32.4 (5.2)	34.3	23.7, 25.2 [b] (3.6)	24.5 [b]
4 [7]	14.2	29.6 (71.8)	122.2 (11.0)	[c]	149.0 —	118.0 (97.5)	24.1 (13.2)	132.1 (81.3)	127.8 (12.5)	129.8 (10.3)	131.4 (2.9)				
8	19.1	39.1 (69.0)	124.1 (20.3)	131.3 (9.3)	139.0	122.8 (92.1)	23.8 (9.6)	~122.6 [d] (~106)	154.9 (12.0)	123.1 (11.2)	153.1	29.8 (4.8)	34.4	23.7, [e] 25.3 [f]	24.6 [e,f]
3 [7]	15.3	35.5 (71.1)	122.8 (19.8)	129.7 (13.9)	143.4	118.5 (93.8)	22.5 (8.8)	132.1 (81.3)	127.8 (12.5)	129.8 (10.3)	131.4 (2.9)				

[a] Carbon atom of the aromatic ring. [b,e,f] May be reversed. [c] Overlapped by the aromatic signals. [d] Partially overlapped.

diagrams, such as HMQC and HMBC spectra. The elemental composition of **7** was proved by HRMS.

The thermolysis of phosphabicyclohexanes is a useful approach for the preparation of dihydrophosphinine oxides.[2–6] To be able to apply this method for the cyclopropane ring opening of dichlorocarbene adducts **6A** and **6B**, their stability was mapped by thermal examinations. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential scanning calorimetry (DSC) measurements showed that opening of the cyclopropane ring of **6A** and **6B** required somewhat more forcing conditions than that of the earlier described phosphabicyclohexanes including *P*-phenyl derivative **2**[4] (142–155 °C *vs.* 122–141 °C). Thermolysis of adduct **6A** at 143 °C resulted in the dihydrophosphinine oxide as a single isomer (**8**) (Scheme 3).



Scheme 3

No traces of the other isomer (**7**) could be detected. This selectivity is surprising, as thermolysis of the earlier phosphabicyclohexanes always afforded the dihydrophosphinine oxides as a mixture of two double-bond isomers.[2,4–6] In the case of the phenyl-phosphabicyclohexane (**2**), isomers **3** and **4** were formed in 72 and 28% yield, respectively (Scheme 1),[4] but the proportion of the isomers was similar in all other instances.[5,6] It was not then surprising that the thermolysis of isomer **6B** also gave dihydrophosphinine **8** selectively (Scheme 3).

The structure of dihydrophosphinine oxide **8** was proved by ^{31}P, ^{1}H and ^{13}C NMR, as well as mass spectroscopic methods. The δ_P of 19.1 falls in the usual range reported for dihydrophosphinine oxides.[4–6] We recall that isomer **7** reveals an anomalous downfield shift of 45.9. The isomeric structure **8** is well established by the ^{3}J(H,H) coupling of 12.7 Hz detected for C_5-H and C_6-H at δ_H 6.70 and 6.41, respectively (Table 3). The ^{13}C NMR spectral parameters of product **8** show close resemblance to those of the *P*-phenyl derivative **3**[7] (Table 2). The mass spectral fragmentation of **8** is similar to that of isomer **7**; in the spectrum of **8**, the molecular ion (*m*/*z* 364) is 57% with M − Cl (*m*/*z* 329) as the base peak, while for **7**, M^+ is the base peak and M − Cl is of 97%. The elemental composition of **8** was confirmed by HRMS.

2. Molecular modelling of the aryl-dihydrophosphinine oxides (3, 4, 7, and 8)

Minimum energy conformations of **3**, **4**, **7** and **8** were calculated by the PM3[15] semiempirical method that is particularly well suited to computation of phosphorus-containing systems.

Table 3 Selected ^{1}H NMR data for dihydrophosphinine oxides **3**, **4**, **7** and **8**

Compound	δ_H, multiplicity (*J* in Hz) C_3-H	C_5-H	C_6-H
7	6.37 s		6.46 d $^{2}J_{PH}$ = 20.9
4 [7]	6.23 dt $^{3}J_{PH}$ = 20.0 $^{3}J_{HH}$ = 7.1		[a]
8		6.70 dd $^{3}J_{PH}$ = 35.0 $^{3}J_{HH}$ = 12.7	6.41 dd $^{2}J_{PH}$ = $^{3}J_{HH}$ = 12.8
3 [7]		6.86 dd $^{3}J_{PH}$ = 35.7 $^{3}J_{HH}$ = 14.0	6.15 dd $^{2}J_{PH}$ = $^{3}J_{HH}$ = 14.0

[a] Overlapped.

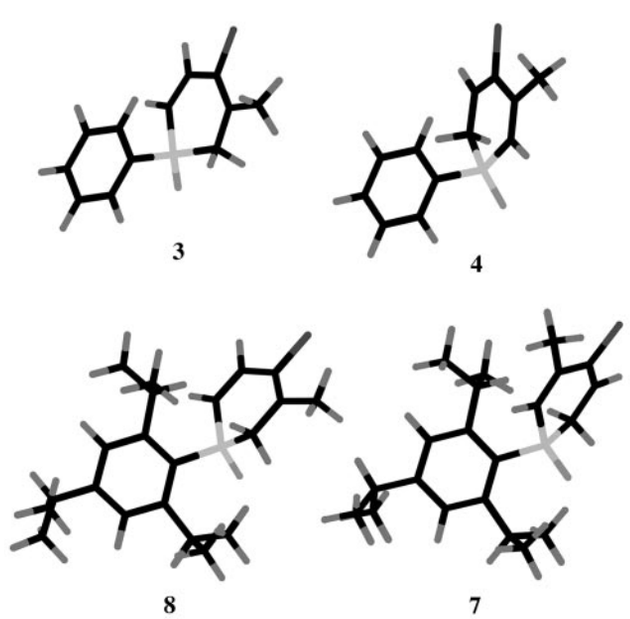


Fig. 1 Minimum energy conformations of **3**, **4**, **7** and **8** obtained by PM3 semiempirical calculations.

Minimum energy conformations are depicted on Fig. 1. Atomic distances between the phosphorus atom and the connected aromatic carbon atom was slightly elongated in **8** (1.872 Å) and **7** (1.877 Å) with respect to that measured in **3** (1.822 Å) and **4** (1.822 Å). The bond stretching can be interpreted on the basis of unfavoured steric interactions due to the *ortho* isopropyl groups. The steric bulk also has a significant effect on the molecular geometry of the *P*-aryl dihydrophosphines **7** and **8**. We defined two descriptors to quantify these changes: the planarity of the dihydrophosphinine ring expressed as the

Table 4 Significant geometrical features of the dihydrophosphinine oxides **3**, **4**, **7** and **8**

Compound	P–(C_2–C_3–C_4–C_5–C_6) distance/Å	RMS for the plane/Å	Aryl ring–hetero ring angle/deg
3	0.232	0.0364	91.1
4	0.220	0.0361	88.6
7	0.456	0.0440	74.2
8	0.517	0.0537	117.9

Table 5 Differences between the electron densities (Δq) and between the NMR chemical shifts ($\Delta\delta$) as a comparison for compound **7** with products **3**, **4** and **8**

Compound	P		C_2		C_6	
	Δq/e	$\Delta\delta$/ppm	Δq/e	$\Delta\delta$/ppm	Δq/e	$\Delta\delta$/ppm
7/3	−0.18	30.6	0.04	−0.3	0.16	−11.4
7/4	−0.16	31.7	−0.15	6.2	−0.12	11.9
7/8	−0.10	26.8	0.12	−3.3	0.08	−7.1

Table 6 ESP atomic charges at P atoms together with the ^{31}P NMR chemical shifts

Compound	q_P/e	δ_P
3	1.83	15.3
4	1.85	14.2
7	2.01	45.9
8	1.91	19.1

height of the phosphorus atom above the plane defined by the other five atoms and also the plane angle measured between the aryl and the dihydrophosphinine rings (Table 4). It is not surprising that we found a straightforward correlation between the planarity of the dihydrophosphinine ring and the size of aromatic *ortho* substituents in the benzene ring. The angles between the aryl and the hetero rings seem, however, to be dependent also on the isomeric structure, at least in the case of the *P*-aryl derivatives (**7** and **8**).

The electronic structure of the dihydrophosphinine ring was also evaluated to try to explain the unusual carbon and phosphorus chemical shifts in **7**. The differences between the δ_P and δ_C values selected, as shown in Table 5, were compared with the corresponding differences in the electrostatically fitted atomic (ESP) charges calculated by the PM3 method. Although the computational results have only qualitative importance, the correlation between the differences in the electron densities and those in the corresponding chemical shifts is considerable (Table 5). Furthermore, atomic charges calculated at the phosphorus atom of the dihydrophosphinines (**3**, **4**, **7** and **8**) correlated well with the ^{31}P NMR chemical shifts detected (Table 6). It is known that an increase in the electron density generally results in a more downfield chemical shift. The increased electron density calculated for the phosphorus atom in **7** is, indeed, in agreement with the unusually downfield ^{31}P NMR chemical shift. Hence our results demonstrate that the ESP charges make an important contribution to the value of the ^{31}P NMR chemical shift and they can therefore be used to aid the interpretation of NMR observations. The unusually high electron density around the phosphorus atom of **7** must be the consequence of the decreased angle of 74.2° that connects the aryl ring to the hetero ring.

The electrostatic potential maps of the van der Waals surface of **4** and **7** were also calculated (see Supplementary material). The negative potential detected around the phosphorus atom of **4** is in agreement with its decreased electron density and suggests the importance of electrostatic effect of the aromatic ring.

The difference observed in the multiplicity of the C_3-H moiety in the ^{1}H NMR spectra of **7** and **4**, can be interpreted on the basis of the corresponding molecular geometries. The $^3J_{HH}$ coupling constants calculated by the method of Altona [16] *et al.* were found to be 6.5 Hz for **4** and 0.5 Hz for **7** (with dihedral angles of 69.8° and 37.8°, respectively) and are in good agreement with the experimentally obtained 7.1 and 0 Hz, respectively.

In the next part of our project, we shall evaluate if the selective transformations are generally applicable to the sphere of 2,4,6-trialkylphenyl dihydrophospholes and phosphabicyclohexanes. The dihydrophosphinines with sterically demanding P-substituents will be utilised in the synthesis of bridged P-heterocycles which are useful in the generation of low-coordinated P-species.

It can be concluded that *Approaches A* and *B* allow selective dichlorocyclopropanation of dihydrophosphole **5** to afford phosphabicyclohexanes **6A** and **6B**, respectively. The outcome of the cyclopropane ring opening of the isomers of **6** depends on the reaction conditions applied; the thermolysis of **6** leads to the sole formation of dihydrophosphinine oxide **8**, while the base-induced ring opening of **6** gives **7** exclusively.

Experimental

The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker DRX-500 instrument operating at 202.4, 125.7 and 500 MHz, respectively and are measured in ppm. Coupling constants *J* are measured in Hz. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. Mass spectra were obtained on a MS-902 spectrometer at 70 eV.

Dihydrophosphole **5** was prepared as described previously.[17]

6,6-Dichloro-1-methyl-3-(2,4,6-triisopropylphenyl)-3-phosphabicyclo[3.1.0]hexane 3-oxide 6A

To the solution of 4.0 g (12.6 mmol) of dihydrophosphole **5** and 0.55 g (2.42 mmol) of triethylbenzylammonium chloride (TEBAC) in 80 cm^3 of abs. chloroform was added dropwise 22 g (0.55 mol) of sodium hydroxide in 25 cm^3 of water. The mixture was stirred on heating for 3 h. After filtration and separation, the organic phase was made up to its original volume and 0.55 g (2.42 mmol) of TEBAC was added. The reaction mixture was treated with a second portion of aqueous sodium hydroxide as above. The solution obtained after filtration and separation was concentrated *in vacuo*. According to ^{31}P NMR, the residue contained 42% of **6A** (δ_P 80.6), 10% of **6B** (δ_P 78.2) and 48% of **7** (δ_P 45.8). Column chromatography (2% methanol in chloroform, silica gel) afforded two fractions. One of them contained compound **7** as the main component (see next paragraph for further utilisation), while the chemical substance in the other oily fraction was **6A** (yield: 1.26 g, 52%). Its purity was indicated by TLC. ^{31}P and ^{13}C NMR, Table 1; ^{1}H NMR ($CDCl_3$) δ 1.09–1.31 (m, 18H, 3 × CH(CH_3)$_2$), 1.48 (s, 3H, C_1-Me), 1.88 (dd, $^3J_{PH}$ = 22.3, $^3J_{HH}$ = 8.0, 1H, C_5-H), 2.43–2.54 (m, 2H, CH_2), 2.62–2.89 (m, 3H, CH_2, $CHMe_2$), 3.48–3.57 (m, 2H, $CHMe_2$), 7.08 (s, 2H, Ar); MS, *m*/*z* (rel. int.) 400 (M^+, 12), 385 (M − 15, 4), 365 (M − 35, 100), 329 (365 − 35 − H, 26), 249 (ArPO − H, 9) (HRMS, M^+_{found} = 400.1433, $C_{21}H_{31}Cl_2OP$ requires 400.1490 for the ^{35}Cl isotopes).

4-Chloro-5-methyl-1-(2,4,6-triisopropylphenyl)-1,2-dihydrophosphinine 1-oxide 7

Repeated column chromatography of the remaining fraction (*ca.* 2 g) from the previous reaction gave 0.99 g (45%) of **7** in a pure form (TLC). Application of a third aqueous sodium hydroxide treatment in the reaction described in the previous paragraph led to an increase of the relative quantity of **7** (91%

according to ^{31}P NMR). ^{31}P and ^{13}C NMR, Table 2; ^{1}H NMR ($CDCl_3$) δ 1.15–1.29 (m, 12H, $CH(CH_3)_2$), 1.33 (d, $J = 6.7$, 6H, $CH(CH_3)_2$), 2.07 (s, 3H, C_5-Me), 2.86 (septet, $J = 6.8$, 1H, $CHMe_2$), 3.04–3.17 (m, 2H, CH_2), 3.53 (septet, $J = 6.4$, 2H, $CHMe_2$), 6.37 (s, 1H, C_3-H), 6.46 (d, $^{2}J_{PH} = 20.9$, 1H, C_6-H), 7.06 (s, 2H, Ar); MS, *m*/*z* (rel. int.) 364 (M^+, 100), 349 (M − 15, 14), 329 (M − 35, 97) (HRMS, $M^{+}_{found} = 364.1681$, $C_{21}H_{30}ClOP$ requires 364.1723 for the ^{35}Cl isotopes).

6,6-Dichloro-1-methyl-3-(2,4,6-triisopropylphenyl)-3-phosphabicyclo[3.1.0]hexane 3-oxide 6B

A mixture of 1.60 g (5.03 mmol) of dihydrophosphole **5**, 0.36 g (1.58 mmol) of TEBAC and 46.8 g (0.252 mol) of sodium trichloroacetate in 200 cm^3 of chloroform was stirred at reflux for 5 days. The contents of the flask were then filtered and the solvent of the filtrate evaporated. The residual oil was purified by repeated column chromatography (1, chloroform, 2, 2% methanol in chloroform, 3, benzene–acetone 4 : 6, silica gel) to furnish 0.95 g (47%) of **6B**; mp 142–144 °C (dec., acetone); ^{31}P and ^{13}C NMR, Table 1; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, $J = 6.0$, 6H, $CH(CH_3)_2$), 1.26–1.37 (m, 12H, $2 \times CH(CH_3)_2$), 1.75 (s, 3H, C_1-Me), 2.09–2.17 (m, 1H, C_5-H), 2.23–2.57 (m, 2H, CH_2), 2.59–2.97 (m, 3H, CH_2, $CHMe_2$), 3.35 (septet, $J = 6.2$, 2H, $CHMe_2$), 7.07 (s, 2H, Ar); MS, *m*/*z* (rel. int.) 400 (M^+, 3), 385 (M − 15, 2), 365 (M − 35, 100), 329 (365 − 35 − H, 45) (Anal. Found C, 62.52, H, 7.51; $C_{21}H_{31}Cl_2OP$ requires C, 62.84, H, 7.73%).

4-Chloro-3-methyl-1-(2,4,6-triisopropylphenyl)-1,2-dihydrophosphinine 1-oxide 8

A 0.48 g (1.20 mmol) sample of adduct **6A** was heated at 140–145 °C in a vial until the evolution of hydrochloric acid ceased (*ca.* 30 min). The crude product was purified by column chromatography (2% methanol in chloroform, silica gel) to provide 0.37 g (85%) of **8** in a pure form (TLC). ^{31}P and ^{13}C NMR, Table 2; ^{1}H NMR ($CDCl_3$) δ 1.12–1.35 (m, 18H, $3 \times CH(CH_3)_2$), 2.08 (s, 3H, C_3-Me), 2.85–3.11 (m, 3H, $CHMe_2$, CH_2), 3.86 (septet, $J = 6.6$, 2H, $2 \times CHMe_2$), 6.41 (dd, $^{2}J_{PH} = {}^{3}J_{HH} = 12.8$, 1H, C_6-H), 6.70 (dd, $^{3}J_{PH} = 35.0$, $^{3}J_{HH} = 12.7$, 1H, C_5-H), 7.10 (s, 2H, Ar); MS, *m*/*z* (rel. int.) 364 (M^+, 57), 349 (M − 15, 13), 329 (M − 35, 100) (HRMS, $M^{+}_{found} = 364.1690$, $C_{21}H_{30}ClOP$ requires 364.1723 for the ^{35}Cl isotopes).

The thermolysis of 0.10 g (0.25 mmol) of adduct **6B** employing the same procedure as for isomer **6A**, afforded 0.07 g (72%) of **8** in a purity of 95%. ^{31}P NMR ($CDCl_3$) δ 19.8.

Details of the PM3 calculations

All calculations were carried out using SPARTAN 3.1 on an SGI R4400 workstation. PM3 calculations were performed on geometries preoptimised by the MM2 molecular mechanics method. Conformational analysis of **3**, **4**, **7** and **8** involved the systematic variation of all rotatable bonds using an increment of 30 deg in combination with Osawa's corner-flapping–bond-flipping algorithm applied for phosphole rings. Low energy conformations were identified by setting the minimum Boltzmann population cut-off to 0.1. The conformations lowest in energy were used for further structural studies.

Supplementary material

Electrostatic potential maps calculated on the van der Waals surface of **4** and **7**. Positive and negative potentials are coloured in red and blue, respectively.†

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