

# Extremely bulky triarylphosphines incorporating 2,6-diisopropylphenyl substituents; consideration of steric shielding and steric pressure

René T. Boéré \*, Yuankui Zhang

Department of Chemistry and Biochemistry, The University of Lethbridge, 4401 University Drive, Lethbridge, AB., Canada T1K 3M4

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This paper is dedicated to Prof. Dr. Konrad Seppelt on the occasion of his 65th birthday

## Abstract

The geometry of 15 triarylphosphines which differ in the nature of the substituents at the 2 and 6 positions of one or more phenyl rings are compared. The sum of angles around phosphorus,  $\sum\{\angle\text{CPC}\}$ , is used as the primary measure of steric bulk. The roles of substituents, which act as *steric shields* surrounding the phosphine lone pair and of those which generate *steric pressure* and cause flattening of the  $\text{C}_3\text{P}$  pyramid are identified. Both crystallographic and computational (HF 6-31G(d)) structures are used to assess  $\sum\{\angle\text{CPC}\}$ , the pyramidalization angle  $\alpha$ , the average C–P distance, and the helical twist angle of the aryl rings  $\beta$ . All of these parameters confirm that *ortho*-2,6-diisopropyl substituted aryl groups generate the most sterically congested triarylphosphines. Comparison to Tolman cone angles are made where these are available.

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## 1. Introduction

The importance of steric protection to modern organophosphorus chemistry is incontrovertible [1]. Since the first report of the stabilization of a P=P bond by Yoshifuji [2] through the use of the “supermesityl” ( $\text{Mes}^*$ ) substituent, i.e. 2,4,6-tri-*tert*-butylphenyl, virtually every advance in low-coordinate low-oxidation state chemistry of the pnictides, and indeed of the rest of the main group elements, has depended in some fashion on the use of bulky substituents acting in some capacity of steric protection [3]. Probably, because the isolation of P=P and Si=Si bonds requires the prevention of oligomerization, the use of bulky substituents is frequently described as “kinetic protection.” However, Burford

et al. [4] have demonstrated conclusively that the stabilization afforded by superbulky substituents is as much thermodynamic as it is kinetic, because the putative oligomeric products are often *destabilized* energetically compared to the unsaturated monomers as a result of increased steric crowding in the oligomers. These workers used quantum-chemical calculations on model systems to demonstrate this effect.

We have been interested in assessing similar thermodynamic and structural “side-effects” of using bulky substituents. It is clear that without superbulky groups, many of the novel architectures of main group elements uncovered during the last 25 years simply could not exist. Yet it is well recognized that these groups do – unavoidably – alter the structure and behaviour of the very compounds they are designed to stabilize. This was particularly appreciated in the early days of research in this area through the frequent comparisons drawn to model systems calculated using quantum mechanics, in

\* Corresponding author. Tel.: +1 403 329 2045; fax: +1 403 329 2057.

E-mail address: [boere@uleth.ca](mailto:boere@uleth.ca) (R.T. Boéré).

which bulky R groups were routinely replaced with a simple hydrogen atom (out of calculational ease or indeed, necessity, since computational resources at the time were not adequate for anything larger) [5]. One of the ways in which we have tried to assess such side effects is to incorporate superbuly substituents in molecules where they are *not* required to prevent oligomerization, such as in unsaturated compounds of the 2nd period elements. We reasoned that such substitution could lead to unexpected structures and reactivity patterns, breathing new life into old functional groups [6]. We therefore attempted the synthesis of a series of homologous heteroallylic systems which differ *only* by the swapping of the Group 15 elements (Scheme 1), so that the effects of substituent size might be separated from those caused by the type of pnictides incorporated in the molecules.

Thus, we are exploring the possible homologous series based on amidines (A) and guanidines (B) by replacement of one or more of the nitrogen atoms with heavier pnictides [6]. Each molecule prepared in this way is in principle also capable of acting as a monoanionic ligand by deprotonation, and hence form potential ligands towards both main group and transition metals [7].

Our choice of a bulky substituent – which by design is to be identical for the whole series – is the 2,6-diisopropylphenyl group (Dipp), which we believe represents a good compromise between the steric demands required by all the group 15 elements. The Mes\* group was found in our hands to be too large to introduce into the parent amidine or guanidine structures (E = N,N). Since our initial work on what at the time were the bulkiest amidines to have been reported [6], there has been an explosion of interest in the chemistry of amidines and their deprotonated amidinate congeners [8], coinciding with the fascinating reports from Jordan on alkene polymerization using dimethylaluminium derivatives of amidines which operate *without* the addition of any transition metals [9]. Similarly, since our report on the bulky guanidine (E = N,N,N) [10], there have been several other reports on bulky guanidine and guanidinate derivatives. We have demonstrated that the presence of these bulky groups – which are completely unnecessary to stabilize the organonitrogen architectures – induces significant differences in the structure and chemical behaviour of

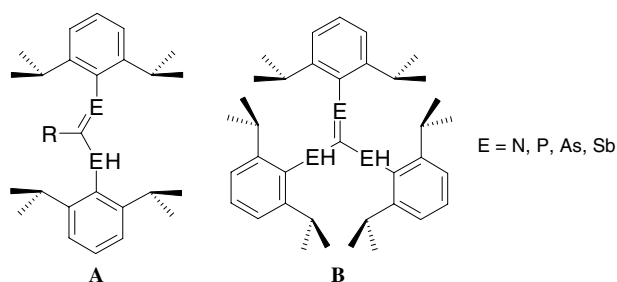
these functional groups in comparison to small organic substituents [6,10].

More recently, we have reported on our first foray into the monophosphorus analogues [11]. Thus examples of monophosphaamidines (E = N,P) and monophosphaguanidines (E = N,N,P) have been prepared and structurally characterized in our laboratories, as well as Li and K complexes of the deprotonated monoanions [12]. In order to pursue these phosphorus derivatives, we required 2,6-diisopropylphenylphosphine derivatives which at the time were unknown, and we have thus reported the synthesis of DippPX<sub>2</sub> derivatives, where X are halogens and hydride [13]. In agreement with results reported for mesityl (2,4,6-trimethylphenyl) and Tripp (2,4,6-triisopropylphenyl) phosphine halides, the products from using Grignard reagents of these bulky aryl groups with PCl<sub>3</sub> inevitably include mixed chloro–bromo phosphines [14].

## 2. Steric effects in triarylphosphines

As an extension to these investigations, we are also studying the chemistry of triarylphosphines incorporating superbuly substituents. Triarylphosphines, and triorganophosphines in general, are extremely important compounds primarily because of their use as ligands in a host of catalytic applications [15]. The current Strem Inc. catalog lists over 150 triorganophosphines for sale, many of them triarylphosphines [16]. The overwhelming importance of: (i) aryl phosphines, with PPh<sub>3</sub> as the world's most common trivalent phosphorus compound, (ii) the fact that the most popular bulky substituents are aryl derivatives, and (iii) the wealth of structural data available for such compounds makes a study of bulky aryl groups on phosphorus of prime significance. In this paper, we report on results from our group in placing three Dipp groups onto one phosphorus atom to create Dipp<sub>3</sub>P [17] and similar results reported recently by Sasaki and Yoshifuji [18] for the closely related Tripp<sub>3</sub>P. We wish to discuss some of the divergent aspects of steric effects that operate on triarylphosphines which we hope will be generalizable to other aspects of organoelement chemistry. In particular, we distinguish between steric effects that are primarily *shielding* in nature and those that are primarily associated with generating steric *pressure*.

The geometry of Dipp<sub>3</sub>P and Tripp<sub>3</sub>P confirm them as the bulkiest triarylphosphines on record. There are several ways to assess this criterion. Traditionally coordination chemists have used the Tolman “cone angle” to assess the steric bulk of a phosphine [19]. The well-known Tolman approach is to view the van der Waal's surface of the phosphine from the perspective of a standard coordinated metal, which is of course of extreme importance when considering phosphine ligands in coordination complexes and in catalytic applications. It is



Scheme 1.

also possible, however, to consider the steric bulk or steric strain at the phosphorus atom, and this is the approach taken here. Perhaps the simplest measure of this latter criterion is to compare the sums of angles around phosphorus, which will be  $360^\circ$  for a trigonal planar geometry – the ultimate limit for a three-coordinate molecule [20] – and about  $328^\circ$  for a pyramidal molecule with “tetrahedral” bond angles. The parent phosphine,  $\text{PH}_3$ , is well known to be much more pyramidal than that, indeed the angle sum  $\sum\{\angle\text{HPH}\} = 280.8$ , and a very high calculated inversion barrier of  $\sim 155 \text{ kJ mol}^{-1}$  is associated with this highly pyramidal structure [21]. For years, the record for steric congestion in a phosphine was held by trimesitylphosphine,  $\text{Mes}_3\text{P}$ , for which  $\sum\{\angle\text{CPC}\} = 329.4^\circ$  [22].

### 3. Methodology

We have selected a set of mono and di *ortho* substituted triarylphosphines for which the crystal structures have been determined. Both symmetrical and asymmetrically substituted examples are included, as listed in

Table 1. Crystal structure data were taken either from unpublished structures from our own laboratory or from the CDC Database (version 5.25, November 2003). In our selection of substituents, we deliberately excluded those for which secondary bonding interactions, such as hydrogen bonding or ionic charges, might reasonably be expected to distort the picture of steric – i.e., non-bonding – interactions. Tri-*ortho*-tolylphosphine, like several other entries in Table 1, crystallizes with two molecules per equivalent position in the unit cell, and one of these has  $\sum\{\angle\text{CPC}\} = 308.3^\circ$ , which is actually larger than the value in triphenylphosphine itself [23]. This raises the issue of whether small changes in this parameter may be affected by crystal packing forces, which can be significant for bond angles. Therefore, we have also calculated the geometries of all 15 examples at the HF 6-31G(d) level of theory using GAUSSIAN 98 [24]. The conformational space of the molecules was thoroughly investigated using molecular mechanics, using the MM+ method as implemented in HYPERCHEM 5.1 [25]. Similar methods have been used previously by others [26]. Subsequently, the most likely geometries were optimized at the semi-empirical PM3

Table 1  
 $\sum\{\angle\text{CPC}\}$  from X-ray diffraction experiments and quantum mechanical calculations

Compound	$\sum\{\angle\text{CPC}\}$	Av. $\angle\text{CPC}$	Av. $\alpha$	Av. P–C	Av. $\beta$	Cone angle	Reference
<i>X-ray crystallographic data</i>							
$\{2-(\text{CH}_3)_2\text{P}-\text{C}_6\text{H}_4\}_3\text{P}$	298.26 <sup>a</sup>	99.42	28.23	1.85	37.94		[37]
$\{2-\text{CN}-\text{C}_6\text{H}_4\}_3\text{P}$	302.56	100.85	27.12	1.83	38.66		[38]
$\{2-\text{CF}_3-\text{C}_6\text{H}_4\}_3\text{P}$	304.38	101.46	26.63	1.84	35.10	205	[28]
$\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}\{\text{C}_6\text{H}_5\}_2\text{P}$	306.47	102.16	26.06	1.83	44.83		[29]
$\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}_3\text{P}$	307.01 <sup>a</sup>	102.34	25.91	1.83	41.61	212	[39]
$\{2-\text{CH}_3-\text{C}_6\text{H}_4\}_3\text{P}$	307.78 <sup>a</sup>	102.59	25.69	1.83	42.18	194	[23]
$\text{PPh}_3$	308.14	102.71	25.59	1.83	35.80	145	[1,27]
$\{2,6-\text{F}_2\text{C}_6\text{H}_3\}_3\text{P}$	309.50	103.17	25.22	1.84	34.31		[40]
$\{\text{C}_6\text{F}_5\}_3\text{P}$	309.94	103.31	25.09	1.83	35.48	184	[41]
$\{2,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_3\}\{\text{C}_6\text{H}_5\}_2\text{P}$	314.68	104.89	23.73	1.84	41.64		[42]
$\{2,6-(\text{CH}_3)_2-\text{C}_6\text{H}_3\}_3\text{P}$	328.57	109.52	19.42	1.84	39.46		[43]
$\{2,4,6-(\text{CH}_3)_3-\text{C}_6\text{H}_2\}_3\text{P}$	329.09 <sup>a</sup>	109.70	19.24	1.83	40.69	212	[22]
$\{9-\text{C}_{14}\text{H}_9\}_3\text{P}$ (anthracyl)	331.21	110.40	18.52	1.83	39.55		[35]
$\{2,4,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_2\}_3\text{P}$	334.41	111.47	17.39	1.84	33.39		[18]
$\{2,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_3\}_3\text{P}$	335.64	111.88	16.94	1.85	32.19	265	[42]
<i>HF 6-31G(d) calculations</i>							
$\{2-\text{CF}_3-\text{C}_6\text{H}_4\}_3\text{P}$	306.90	102.30	25.94	1.86	34.11	205	This work
$\{2-\text{CN}-\text{C}_6\text{H}_4\}_3\text{P}$	307.34	102.45	25.82	1.85	41.30		This work
$\{2-(\text{CH}_3)_2\text{P}-\text{C}_6\text{H}_4\}_3\text{P}$	308.70	102.90	25.44	1.86	37.10		This work
$\text{PPh}_3$	310.00	103.33	25.07	1.84	35.66	145	This work
$\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}\{\text{C}_6\text{H}_5\}_2\text{P}$	310.18	103.39	25.02	1.84	36.74		This work
$\{2-\text{CH}_3-\text{C}_6\text{H}_4\}_3\text{P}$	310.59	103.53	24.91	1.85	39.98	194	This work
$\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}_3\text{P}$	310.76	103.59	24.86	1.85	39.29	212	This work
$\{\text{C}_6\text{F}_5\}_3\text{P}$	314.54	104.85	23.78	1.84	26.66	184	This work
$\{2,6-\text{F}_2\text{C}_6\text{H}_3\}_3\text{P}$	315.46	105.15	23.50	1.84	26.55		This work
$\{2,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_3\}\{\text{C}_6\text{H}_5\}_2\text{P}$	318.66	106.22	22.55	1.85	39.97		This work
$\{2,4,6-(\text{CH}_3)_3-\text{C}_6\text{H}_2\}_3\text{P}$	330.33	110.11	18.82	1.85	38.18	212	This work
$\{2,6-(\text{CH}_3)_2-\text{C}_6\text{H}_3\}_3\text{P}$	330.51	110.17	18.76	1.86	38.27		This work
$\{9-\text{C}_{14}\text{H}_9\}_3\text{P}$	334.10	111.37	17.50	1.86	36.17		This work
$\{2,4,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_2\}_3\text{P}$	336.80	112.30	16.50	1.87	32.00		This work
$\{2,6-[(\text{CH}_3)_2\text{CH}]_2-\text{C}_6\text{H}_3\}_3\text{P}$	337.01	112.34	16.43	1.87	32.29	265	This work

<sup>a</sup> Two independent molecules in the unit cell.

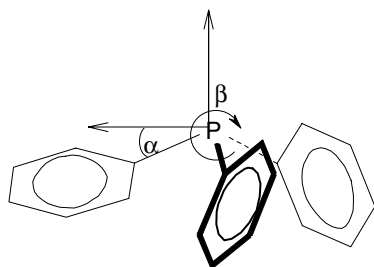
level (also in HYPERCHEM), and the lowest-energy conformer geometries from the PM3 minimization were used as input to the HF calculations. In each case, a stationary point was located in the HF calculations. The large size of the molecules precluded performing frequency calculations, which in part was the reason for first conducting a thorough semi-empirical search of their conformation spaces.

As an alternative to the  $\sum\{\angle\text{CPC}\}$  to describe the geometry at phosphorus, other workers have defined a pyramidalization angle  $\alpha$ , which refers to the angle by which a single C–P bond is bent down from the horizontal in a perpendicular fashion (Scheme 2) [26]. Hence an alpha angle of  $0^\circ$  represents a completely flat  $\text{EX}_3$ , while the ideal tetrahedral molecule has  $\alpha = 19.4^\circ$  and the parent phosphine  $\text{PH}_3$  has  $\alpha = 32.7^\circ$ .

The  $\alpha$  value is a simple and visually appealing way to describe pyramidalization at phosphorus, and is readily calculated from a conventional Z-matrix as used in many computational packages. On the other hand, this parameter is not directly available from archival crystal data, and neither is it as conveniently available from modern computational software employing internal coordinates. In both cases, it is much easier to evaluate the angles around phosphorus, from which  $\sum\{\angle\text{CPC}\}$  can be calculated. The  $\alpha$  angle is also not readily defined for phosphines bearing more than one kind of substituent. We have therefore determined and included in Table 1 an average value of  $\alpha$  calculated from  $\sum\{\angle\text{CPC}\}$  using the following trigonometric relationship:

$$\alpha = \cos^{-1} \left[ \frac{\sin(\sum \angle\text{CPC})}{6 \cdot \cos 30^\circ} \right].$$

Since the steric pressure exerted by the substituents (including H) at the *endo* positions are expected to differ depending on the relative orientation of the aryl rings, we have also recorded the average torsional angles  $\beta$  which we define as the dihedral angle between the 3-fold axis of the phosphine and the  $\text{C}_2$  atom of the aryl ring.  $\beta$  is  $0^\circ$  for aryl rings parallel to, and  $90^\circ$  for rings perpendicular to the 3-fold axis. (We have not distinguished between negative and positive values for this angle, which corresponds to distinguishing enantiomeric pairs.) The C–P bond lengths, likewise, may reflect the degree of ste-



Scheme 2.

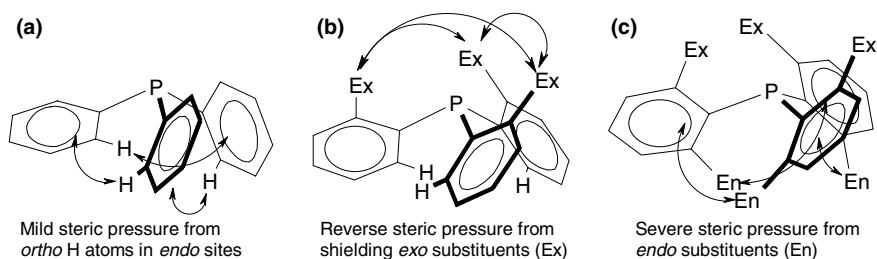
ric crowding at the P atom. All of these parameters are listed in Table 1.

#### 4. Results and discussion

Triphenylphosphine is by far the most common and most heavily used phosphine – the common “benchmark” for phosphine chemistry – and of much greater importance than  $\text{PH}_3$ . In this molecule,  $\sum\{\angle\text{CPC}\} = 308.23^\circ$  [1,27], corresponding to an average CPC bond angle of  $102.7^\circ$ . Thus the replacement of the small hydrogen atom of  $\text{PH}_3$  by an aryl group causes considerable structural distortion at the phosphorus atom. Furthermore, triphenylphosphine in both the parent structure and in its myriads of derivatives adopts the interleaved phenyl ring “propeller” geometry to minimize the steric repulsion exerted by the ring atoms in non-bonded contacts with the other rings on the same molecule. We conclude that the necessity of accommodating the three planar phenyl rings around the phosphorus centre places a mild but significant amount of steric pressure on the  $\text{Ar}_3\text{P}$  geometry (Scheme 3a) [3a]. Consideration of molecular models indicates this pressure is primarily due to the interaction of the *endo* set of *ortho* hydrogen atoms with the carbon atoms of a neighbouring phenyl ring.

On the Tolman “cone angle” scale [19], phosphines with three *ortho* substituents on the aryl rings are ranked as very bulky, so long as these substituents point in the direction of the phosphorus lone pair. This orientation has been defined as the *exo*<sub>3</sub> conformation [28], and is commonly seen in the crystal structures of free *ortho*-substituted arylphosphines, including all those listed in Table 1. NMR measurements confirm that this is also the geometry retained as the major conformer in solution for some of them [29]. In their metal complexes, they sometimes retain this *exo*<sub>3</sub> conformation [30], but in other cases one of the three rings rotates back to an *exo*<sub>2</sub>*endo* conformation [31]. This latter conformation is the required intermediate in Mislou’s two-ring-flip mechanism for substituent interconversion at propeller-like molecules [32]. In the predominant *exo*<sub>3</sub> conformation, the three substituents indeed act as steric shields (Scheme 3b), and impart the large Tolman cone angle to these phosphines if they retain the *exo*<sub>3</sub> conformation in their metal complexes.

However, despite this acknowledged “steric bulk”, we note that these substituents appear to have the effect of compressing the angles around phosphorus because of reverse steric pressure generated between the three *exo*-groups and between them and the phosphorus atom (e.g., in tri-*ortho*-tolylphosphine, the non-bonding methyl H to P atom distance is 2.490 Å, while the non-bonding contact between H atoms on adjacent methyl groups is 3.25 Å). To illustrate this mild reverse steric pressure, in the series  $\text{PPh}_3$ ,  $\{2\text{-CF}_3\text{-C}_6\text{H}_4\}_3\text{P}$  and



Scheme 3.

$\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}_3\text{P}$ ,  $\sum\{\angle\text{CPC}\}$  decreases from  $308.23^\circ$  down to  $304.35^\circ$  (crystallographic values). However, as the results in Table 1 clearly show, the ordering of this sequence obtained from the quantum calculations is different from that obtained from crystallographic values. Consideration of the variation in the twist angle  $\beta$  between the two sets of data indicates that the *average* ring twist is about the same by calculation and experiment; however in the solid state there is much greater variation in this value, ranging from a low of  $\beta = 4^\circ$  to a high of over  $60^\circ$ . Thus, while reverse steric pressure does seem to operate, the effect is small and is apparently compensated for by adjustment of ring conformations to achieve the lowest energy state.

On the other hand, if *both ortho* sites are occupied on the aryl rings, very strong steric pressure is generated (Scheme 3c) at the *endo* set. This steric pressure is associated with a significant increase in  $\sum\{\angle\text{CPC}\}$  and concomitant flattening of the phosphine pyramids. The expected trend is indeed observed – although there are distinct ripples – when the series  $\text{PPh}_3$ ,  $\{\text{C}_6\text{F}_5\}_3\text{P}$ ,  $\{2,4,6-(\text{CH}_3)_3-\text{C}_6\text{H}_2\}_3\text{P}$ ,  $\{9-\text{C}_{14}\text{H}_9\}_3\text{P}$  (anthracyl), and  $\text{Tripp}_3\text{P}/\text{Dipp}_3\text{P}$  is considered, where  $\sum\{\angle\text{CPC}\}$  increases to a top value of  $334.4^\circ$  [33]. Here, there can be no doubt about the results, as the trend from experiment and calculation is highly similar. We note that both by experiment and calculation, the species  $\text{Dipp}_3\text{P}$  and  $\text{Tripp}_3\text{P}$  have the largest expansion of the C–P–C angles, followed closely by (9-anthracyl) $_3\text{P}$ .

The difference between steric shielding and steric pressure is dramatically illustrated in Fig. 1, which depicts space-filling models of tri-*ortho*-isopropylphenylphosphine,  $\{2-(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4\}_3\text{P}$ , and  $\text{Dipp}_3\text{P}$  side by side. While both structures have the same set of three *exo* isopropyl groups in a shielding array, it is clear that in  $\text{Dipp}_3\text{P}$  the shields are pushed in much closer to the phosphorus lone pair. Hence the degree of steric *shielding* asserted by the *exo* substituents is in fact influenced by the amount of steric *pressure* exerted by the *endo* substituents. Striking confirmation of these factors is provided by the recent report of *tris*(3,5-(*bis*-2,6-diisopropylphenyl)phenyl)phosphine, which has *Dipp* groups at both *meta* sites of the aryl rings [34]. The *exo* set of three *Dipp* groups in this molecule generates a large amount of steric shielding to the phosphorus lone pair, but the *endo* set generates almost no steric pressure; indeed  $\sum\{\angle\text{CPC}\} = 309.5^\circ$ , which is only one degree larger than that of  $\text{PPh}_3$ . Thus, while the Tolman cone angle of this phosphine at  $206^\circ$  is definitely large, it is still much smaller than the  $\sim 265^\circ$  that we have calculated for  $\text{Dipp}_3\text{P}$ .

The almost absurdly large value of the Tolman cone angle for  $\text{Dipp}_3\text{P}$  is, however, fully consistent with the fact that we have yet to prepare any metal complexes of this overcrowded phosphine. Indeed, in  $\text{Dipp}_3\text{P}$  the significant steric shield provided by three flanking isopropyl groups has been closed in around the phosphorus lone pair. The contrasting situation shown in Figs.

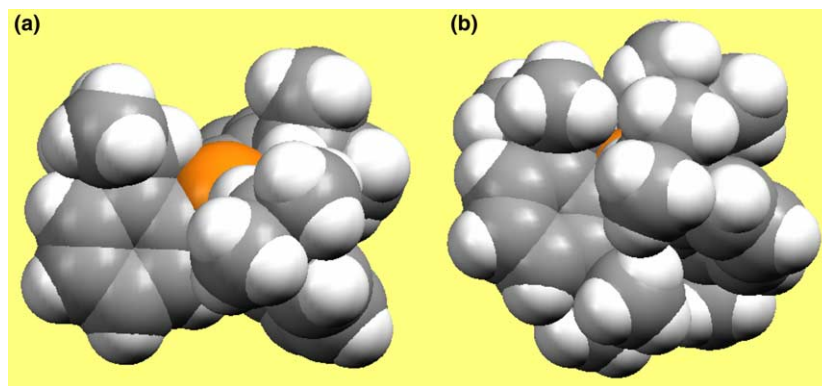


Fig. 1. Space-filling diagram of (a) tri-*ortho*-isopropylphenyl phosphine and (b)  $\text{Dipp}_3\text{P}$ . Care has been taken to ensure that the same enantiomer of each structure has been plotted and that the molecules are in the same relative orientation. The structures are taken from crystallographic data. Similar results are obtained from quantum calculations.

1(a) and (b) bears a strong resemblance to the opening and closing of a flower bud. Thus while steric shielding and steric pressure are distinct factors in triarylphosphines, they can operate symbiotically to provide superb shielding environments for the phosphorus lone pair.

## 5. Conclusions and work in progress

Using the criteria introduced in this work, both from experiment and calculation, we can unambiguously identify the world's most crowded triarylphosphines as those with two *ortho* isopropyl groups, with as a close second the rigid 9-anthracyl group [35]. We note that the 1,8 C–H groups in the latter occupy the same positions that the methine C–H units of the isopropyl groups do, which readily accounts for their similarity in generating steric pressure.

Studies on both the structural and electronic properties of Dipp<sub>3</sub>P are currently underway in our laboratory. Dynamic NMR measurements are being taken to probe the mechanisms of isopropyl group inter-conversion, which appears to operate by either a 2-ring flip or by pyramidal inversion. Fluorescence measurements put an upper limit on the inversion barrier of Dipp<sub>3</sub>P at ~84 kJ mol<sup>-1</sup>, considerably smaller than the 128 kJ mol<sup>-1</sup> calculated for Ph<sub>3</sub>P [36]. The effects of pyramidal flattening with concomitant rehybridization of the phosphorus atom, and of substituent inductive electronic influence on the electrochemical oxidation potentials of phosphines with 2,6-diisopropylphenyl substitution are also under investigation. These results will be published in due course.

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