

# Intramolecular and supramolecular geometry of coordinated $\text{PPh}_3$

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Received 25th November 1999, Accepted 22nd March 2000

Published on the Web 25th April 2000

We report an analysis of the  $\text{M-PPh}_3$  groups in the Cambridge Structural Database. About 60% of the 8663 characterised  $\text{M-PPh}_3$  groups do not exhibit the conformation of a threefold rotor. The  $\text{M-PPh}_3$  moiety occurs with a variety of conformations for the phenyl rings, ranging from the expected threefold rotor, through conformations where the phenyl rings are parallel or orthogonal to the  $\text{P-M}$  vector, to conformations where two rings have approximately equal and opposite  $\text{M-P-C-C}$  torsional angles and are like a flipper rather than a rotor. There are two sub-groups of flipper, in which the third phenyl ring is either approximately parallel or orthogonal to the  $\text{P-M}$  vector. The rotor conformation of  $\text{M-PPh}_3$ , and both forms of the flipper conformation, are capable of forming the sixfold phenyl embrace (6PE), in which all six phenyl rings participate, but only the rotor-6PE possesses the concerted cycle of six local edge-to-face  $\text{Ph}\cdots\text{Ph}$  interactions. The occurrence of fourfold phenyl embraces in  $\text{M-PPh}_3$  compounds is also investigated. Calculated supramolecular energies are presented: a pair of embracing  $\text{PPh}_3$  ligands has a strong supramolecular attractive energy, ranging from  $-11$  to  $-5$   $\text{kcal mol}^{-1}$ .

## Introduction

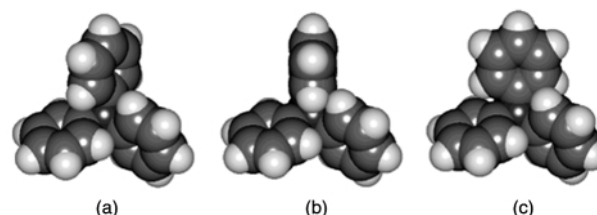
We have previously reported that many crystalline compounds containing  $[\text{Ph}_4\text{P}]^+$  or  $\text{M-PPh}_3$  display multiple phenyl embraces as a predominant supramolecular motif.<sup>1-7</sup> Multiple phenyl embraces involve two or more phenyl groups on each molecule, engaged in intermolecular edge-to-face (ef) and offset face-to-face (off) local interactions, often in concert, and with net attraction. The most commonly occurring embrace is the sixfold phenyl embrace, or 6PE, where the six phenyl rings participate in a concerted cycle of six attractive edge-to-face interactions. The ideal symmetry for this embrace is  $\bar{3}$ , and this exact symmetry occurs in the diverse group of compounds which crystallise with the hexagonal array of sixfold phenyl embraces, the HA6PE lattice.<sup>8-10</sup>

While it was recognised from the outset that coordinated  $\text{PPh}_3$  could be involved in the 6PE,<sup>1</sup> we also noted that most of the compounds in the CSD which include  $\text{M-PPh}_3$  do not form the high symmetry HA6PE lattice type. This could arise because molecules containing  $\text{M-PPh}_3$  have reduced symmetry, or because the  $\text{M-PPh}_3$  has less than the pseudo-threefold local symmetry which might be expected. We have therefore undertaken an analysis of the geometry of coordinated  $\text{PPh}_3$ , reported here. The objectives of this work are to characterise fully the basic intramolecular geometry and conformations of coordinated  $\text{PPh}_3$ , and the types of multiple phenyl embraces adopted by coordinated  $\text{PPh}_3$ . This is preparatory to a description of extended nets of multiple phenyl embraces between compounds with  $\text{PPh}_3$  ligands, in the following paper.<sup>11</sup>

## Results

Our analysis is based on the 8663 independent  $\text{M-PPh}_3$  groups from 5089 structures reported with coordinates in the Cambridge Structural Database<sup>12,13</sup> (CSD v5.17a, April 1999). In these, the  $\text{M-P-C}$  angles average  $115^\circ$ , higher than the tetrahedral value, and the  $\text{C-P-C}$  angles average  $104^\circ$ . The three phenyl rings of  $\text{M-PPh}_3$  are, therefore, closed up slightly, relative to  $[\text{Ph}_4\text{P}]^+$ .

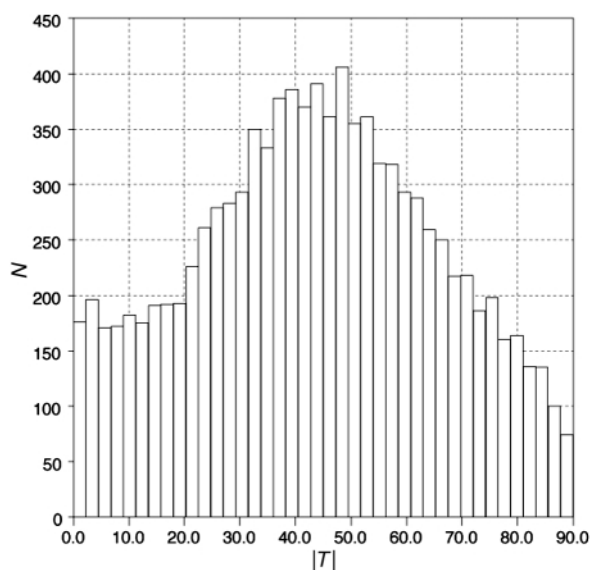
The conformations of the phenyl rings in  $\text{M-PPh}_3$  influence the ability of  $\text{M-PPh}_3$  to engage in multiple phenyl embraces.



**Fig. 1** (a) The rotor conformation of  $\text{M-PPh}_3$  viewed along the  $\text{P-M}$  bond. (b) One phenyl ring in the parallel conformation. (c) One phenyl ring in the orthogonal conformation.

Therefore, we focus on the  $\text{M-P-C-C}$  torsion angles. Bye, Schweizer and Dunitz<sup>14</sup> have investigated the conformations of the phenyl rings in triphenylphosphine oxide,  $\text{OPPh}_3$ , and related compounds, in the context of the geometry of the pathway for conformational inversion,<sup>15</sup> and have formulated the analysis of torsion angles in a slightly different manner.

We examined the expectation that the conformation of  $\text{M-PPh}_3$  would generally approach a rotor with pseudo-threefold symmetry. The rotor conformation has all three phenyl rings twisted around their  $\text{P-C}_{\text{ipso}}$  bond in the same sense relative to  $\text{M-P}$  [see Fig. 1(a)]. Each ring has two  $\text{M-P-C}_{\text{ipso}}-\text{C}$  torsion angles, which ideally differ by  $180^\circ$ . In practice, the deviation from this ideal is frequently up to  $10^\circ$  and occasionally more. This deviation arises because the phenyl ring is not exactly planar but, for the purposes of our analysis, this factor was considered minor and was ignored. For each triphenylphosphine we selected the three  $\text{M-P-C}_{\text{ipso}}-\text{C}$  torsion angles ( $T_i$ ,  $i = 1-3$ ) which were in the range  $-90$  to  $+90^\circ$ , and they were ordered so that  $T_1 < T_2 < T_3$ . An  $\text{M-PPh}_3$  group with rotor conformation would have three torsion angles of the same sign and, ideally, all of the same magnitude. We inquired whether this would be a common arrangement, and whether there would be a preferable torsion angle for the rotor, defining a most favourable conformation. A change in the sign of all three torsion angles for a particular  $\text{M-PPh}_3$  is inversion of the helical chirality: about 90% of  $\text{M-PPh}_3$  structures crystallise in centrosymmetric space groups and, therefore, contain both enantiomers of  $\text{M-PPh}_3$ .



**Fig. 2** Histogram of the magnitudes of 10000 M-P-C<sub>ippso</sub>-C torsion angles,  $T_i$ , for M-PPh<sub>3</sub> entities in the Cambridge Structural Database.

The first question concerned the extent of twist of individual phenyl rings in M-PPh<sub>3</sub>. A histogram of 10000 M-P-C<sub>ippso</sub>-C torsion angles is shown in Fig. 2. The absolute value of each has been taken to simplify the plot and, therefore, all angles lie in the range 0–90°. There is a peak centred at about 45° but, surprisingly, the values cover the entire range from 0 to 90°. The bell-shaped curve is skewed to low angles, so that there are significantly more torsion angles around 0 than around 90°.

The concept of rotor conformation for PPh<sub>3</sub> is less relevant when there are phenyl rings with torsion angles near 0 or 90°. We label an individual ring with torsion angle  $T$  in the range 0–20° as parallel, since it lies (nearly) in the same plane as M-P-C [see Fig. 1(b)], and an individual ring with  $T$  in the range 70–90° as orthogonal [see Fig. 1(c)]. M-PPh<sub>3</sub> entities with one or more torsion angles near 0 or 90° are classified as non-rotors.

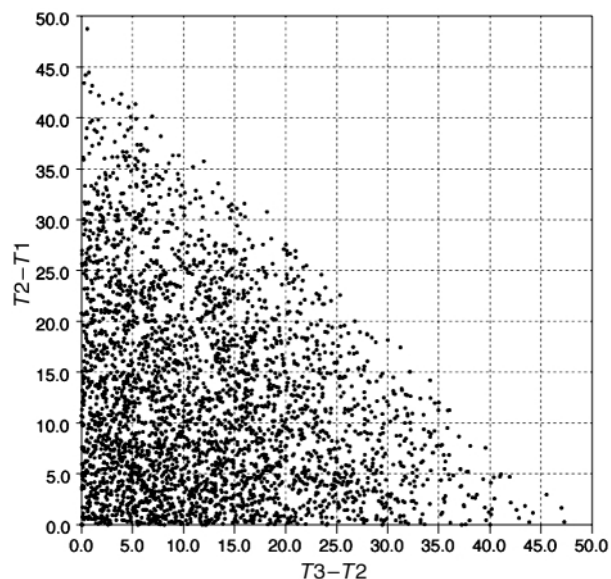
Of the 8663 M-PPh<sub>3</sub> groups in the CSD, 3462 are considered to be acceptable rotors, with all three torsion angles in the range 20–70° (absolute values), and all with the same sign. This leaves 5201 which are not.

Of these 5201, 16 have their three torsion angles lying between 20 and 70°, but not all of the same sign. These are called anti-rotors. The remainder have one or more torsion angles lying outside the 20–70° range, *i.e.* one or more rings are either parallel or orthogonal. 4188 M-PPh<sub>3</sub> groups have at least one parallel ring and 2984 have at least one orthogonal ring. 2810 have a combination of at least one parallel ring with at least one orthogonal ring. The occurrence of a pair of parallel rings or a pair of orthogonal rings on a single ligand is rare, with only 101 and 21 instances, respectively. It should be noted that the signs of  $T_i$  which are near to either 0 or 90° are of little relevance. For example, the difference in orientation for rings with  $T = -10$  or  $+10$ ° is minor, and has negligible influence on the supramolecularity of the ligand.

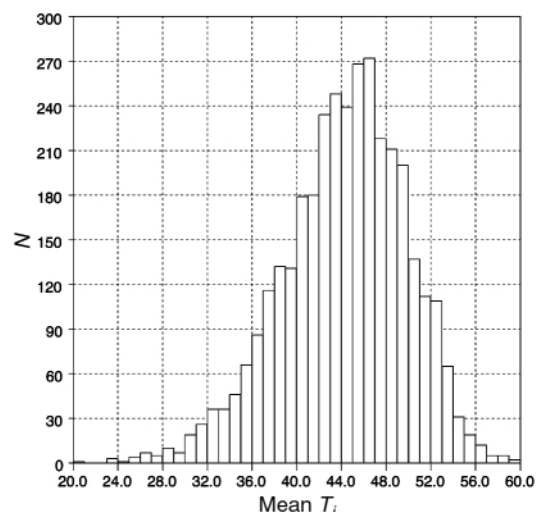
We will now analyse, in turn, each of the major conformation types for M-PPh<sub>3</sub>.

### Good rotors

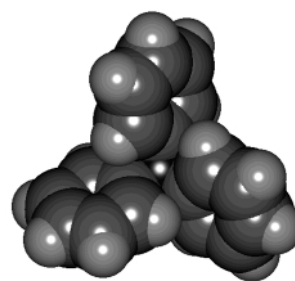
For the ideal threefold rotor, the three  $T_i$  values should be the same. A measure of the deviation of the rotors from this ideal is shown in the scattergram (see Fig. 3) of  $T_2 - T_1$  vs.  $T_3 - T_2$  for the set of 3462 good rotors. If the  $T_i$  values are equal, this conformation should be represented by a point at the origin. While there is a concentration of points at and around the origin of Fig. 3, it is clear that there are many points which deviate markedly from the ideal.



**Fig. 3** Scattergram of the differences in torsional angles,  $T_2 - T_1$  vs.  $T_3 - T_2$ , for the 3462 M-PPh<sub>3</sub> groups classified as good rotors.

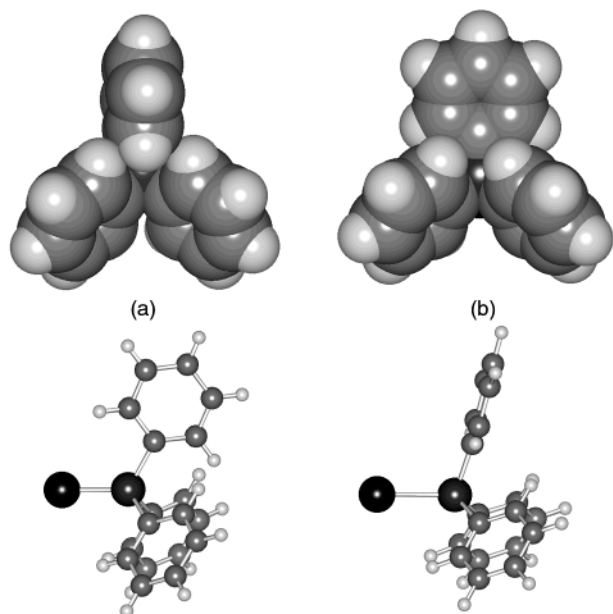


**Fig. 4** Histogram of the average  $|T_i|$  for each M-PPh<sub>3</sub> included in the set of good rotors.

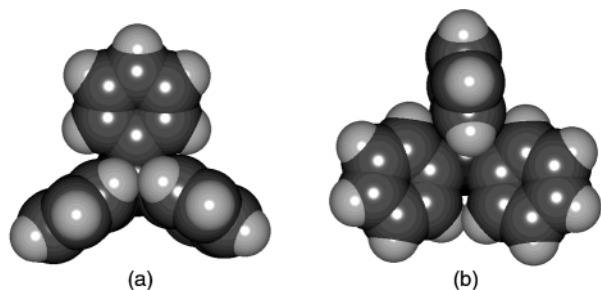


**Fig. 5** The ideal threefold rotor for M-PPh<sub>3</sub> which occurs in (Ph<sub>3</sub>P)Cu(μ-SPh)<sub>3</sub>U(μ-SPh)<sub>3</sub>Cu(PPh<sub>3</sub>)·6thf [YIRHOW].

Fig. 4 indicates the magnitudes of the  $T_i$ , as the average  $|T_i|$  for each M-PPh<sub>3</sub> classified as a good rotor. The mean of the average  $|T_i|$  is 44°, but it is clear that there is a wide range of observed values. Nevertheless, we can describe the ideal threefold rotor for M-PPh<sub>3</sub> which would have  $T_i = 44$ ° for all  $i$ . A view of one such rotor which occurs in (Ph<sub>3</sub>P)Cu(μ-SPh)<sub>3</sub>U(μ-SPh)<sub>3</sub>Cu(PPh<sub>3</sub>)·6thf (CSD refcode [YIRHOW]) where  $T_i = -43.8$ ° for all  $i$ , is given in Fig. 5. This molecule has overall  $D_{3h}$  symmetry and forms a HA6PE lattice.



**Fig. 6** Views of M-PPh<sub>3</sub> ligands in the parallel flipper (a) and orthogonal flipper (b) conformations. The compounds are: (a) (Ph<sub>3</sub>P)<sub>3</sub>-Rh(μ-CO<sub>3</sub>)Rh(PPh<sub>3</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> [CBTPRH],  $T_i = -41, 3, 34^\circ$ , and (b) (Ph<sub>3</sub>P)<sub>2</sub>WCl<sub>3</sub>(NPh)·toluene [CAYPEX],  $T_i = -30, 35, 90^\circ$ .



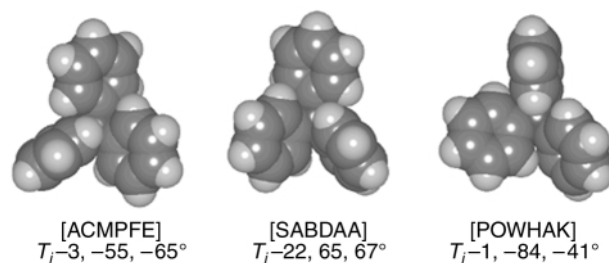
**Fig. 7** (a) An M-PPh<sub>3</sub> in flipper conformation with two parallel phenyl rings and one orthogonal phenyl ring, (Ph<sub>3</sub>P)<sub>2</sub>PdCl[8-(methylthio)theophylline] [NITCIC]. (b) An M-PPh<sub>3</sub> in flipper conformation with one parallel phenyl ring and two orthogonal phenyl rings, (Ph<sub>3</sub>P)W(CO)<sub>3</sub>{B<sub>8</sub>H<sub>8</sub>[C(CH<sub>3</sub>)<sub>2</sub>B(2-methoxybenzyl)]} [SOYPAX].

### Non-rotors: the flipper conformations of M-PPh<sub>3</sub>

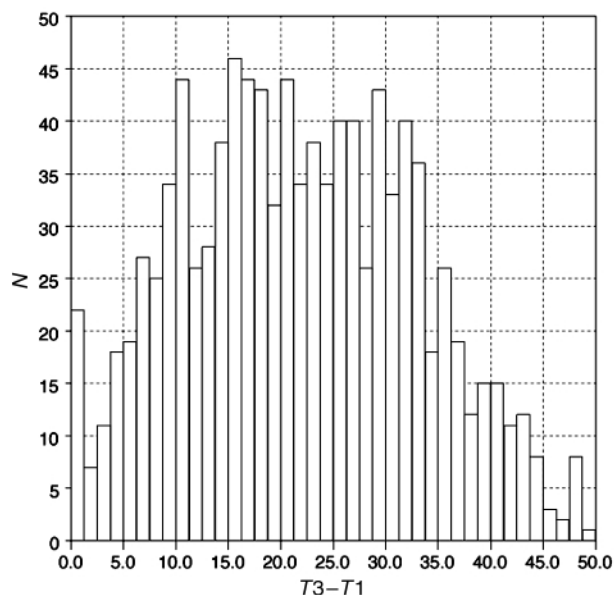
We now move to those M-PPh<sub>3</sub> groups which include at least one parallel ring ( $|T_i| < 20^\circ$ ) or one orthogonal ring ( $|T_i| > 70^\circ$ ). There is a subset of these conformations where the remaining two torsion angles are approximately equal, but of opposite sign. These M-PPh<sub>3</sub> groups possess approximate mirror symmetry, which relates the two non-parallel or non-orthogonal rings. We have termed this conformation the flipper because the two rings with approximately equal and opposite torsional angles present like a flipper. The descriptors parallel and orthogonal further describe the flipper group according to the orientation of the third ring. An example of each is shown in Fig. 6. The criterion used for the flipper conformation is that one of the  $|T_i|$  values is either 0–20° or 70–90° and the  $T_i$  values for the mirror-related rings differ in magnitude by no more than 20°.

There are a few examples of flippers which contain two parallel and one orthogonal ring, such as (Ph<sub>3</sub>P)<sub>2</sub>PdCl[8-(methylthio)theophylline] [NITCIC] which has torsion angles of 2, 6 and 86° [see Fig. 7(a)]. Also occurring, albeit rarely, are examples of flippers with one parallel and two orthogonal rings, such as (Ph<sub>3</sub>P)W(CO)<sub>3</sub>{B<sub>8</sub>H<sub>8</sub>[C(CH<sub>3</sub>)<sub>2</sub>B(2-methoxybenzyl)]} [SOYPAX] [see Fig. 7(b)] with torsion angles of –84, 7 and 81°.

There are about 400 flippers for M-PPh<sub>3</sub> groups in the CSD. This leaves about 4800 ligands (about 55%) where the conform-



**Fig. 8** Representative irregular conformations of M-PPh<sub>3</sub> in (Ph<sub>3</sub>P)-Fe(CO)(COCH<sub>3</sub>)(η<sup>5</sup>-1-methyl-3-phenylcyclopentadienyl)·C<sub>6</sub>H<sub>6</sub> [ACMPFE],  $T_i = -3, -55, -65^\circ$ ; (Ph<sub>3</sub>P)<sub>2</sub>RhH(B<sub>10</sub>H<sub>10</sub>Te)·0.5cyclohexane [SABDAA],  $T_i = -22, 65, 67^\circ$ ; and [*cis*-(Ph<sub>3</sub>P)<sub>2</sub>PtL](BPh<sub>4</sub>)·0.25Me<sub>2</sub>CO [L = *N*-amino(methoxy)methylene-guanidine] [POWHAK],  $T_i = -1, -84, -41^\circ$ .



**Fig. 9** Histogram of  $T_3 - T_1$  for M-PPh<sub>3</sub> groups which form acceptable 6PEs according to the usual criteria.

ation is neither a good rotor, nor a good flipper. Fig. 8 shows three of these.

### The occurrence of 6PEs

Having demonstrated that the M-PPh<sub>3</sub> group is less conformationally regular than expected, and that the threefold rotor conformation is not a major conformation, we now evaluate the participation of M-PPh<sub>3</sub> groups in the sixfold phenyl embrace motif, which in its idealised form has  $\bar{3}$  symmetry. The sixfold phenyl embrace (6PE) is composed of a cycle of six edge-to-face phenyl···phenyl interactions in the domain between the two P atoms. For M-PPh<sub>3</sub> compounds, the P···P separation can be up to 7.5 Å and the P–M vectors are approximately parallel and approximately collinear. In the  $\bar{3}$  ideal the two groups are related by a centre of inversion and so the  $T_i$  values would be + $x, +x, +x$  and – $x, -x, -x$ .

In the CSD, there are 1178 examples of M-PPh<sub>3</sub> intermolecular pairs which form 6PEs according to the criteria (i) P···P < 7.5 Å, (ii) both M–P···P angles in the range 160–180°, and (iii)  $T_i$  values all the same sign and in the range 20–70°. This set contains good 6PEs, but few approach the ideal. For this set, the histogram of  $T_3 - T_1$  (which for a perfect rotor should be 0°) is shown in Fig. 9. For this same set, a histogram of the mean absolute torsional angle has a peak at about 50°, so an ideal 6PE would be like that for (Ph<sub>3</sub>P)Os(CO)<sub>3</sub>(PPh<sub>3</sub>) [COSPHP], torsion angles 50, 50, 50°, shown in Fig. 10. For this, and some other embraces mentioned below, we have calculated the intermolecular energy (see section below on energies for the methodology), and a compilation of the various

**Table 1** Calculated energies for the various 6PE and P4PE depicted in Figs. 10–12, 14 and 16. First, the overall energy is given for the  $(\text{PPh}_3)_2$  pair, and the two components—van der Waals and coulombic—are given in parentheses. This is followed by a  $3 \times 3$  matrix of the individual components of the total energy for each  $\text{Ph} \cdots \text{Ph}$  pair

#### Sixfold phenyl embraces

[COSPHP]:  $-11.3 \text{ kcal mol}^{-1}$  ( $-11.2, -0.1$ )

	1	2	3
1	-0.2	-1.6	-1.6
2	-1.6	-0.2	-1.6
3	-1.6	-1.6	-0.2

[BIVRUT]:  $-7.3 \text{ kcal mol}^{-1}$  ( $-7.9, 0.6$ )

	1	2	3
1	-0.1	-1.1	-0.1
2	-1.4	-0.2	-1.1
3	-0.4	-1.4	-0.1

[CAYPEX]:  $-10.2 \text{ kcal mol}^{-1}$  ( $-9.7, -0.4$ )

	1	2	3
1	-1.7	-0.3	-0.1
2	-1.0	-3.0	-0.2
3	0.7	-3.3	-1.9

[FOMDEQ]:  $-7.0 \text{ kcal mol}^{-1}$  ( $-7.3, 0.2$ )

	1	2	3
1	-0.3	-2.0	-1.2
2	-2.0	-0.3	0.7
3	-1.2	0.7	-0.1

[RABFIJ]:  $-7.8 \text{ kcal mol}^{-1}$  ( $-8.1, 0.4$ )

	1	2	3
1	-1.2	-0.2	-0.1
2	-1.6	-0.2	-0.2
3	-0.2	-1.6	-1.2

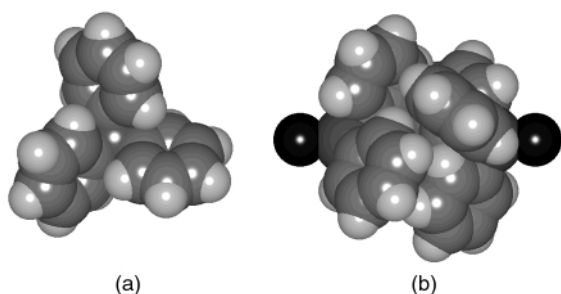
#### Fourfold phenyl embraces

[BEBKIC]:  $-4.6 \text{ kcal mol}^{-1}$  ( $-4.4, -0.2$ )

	1	2	3
1	-1.6	-0.1	0
2	-0.4	-1.6	0
3	0	0	0

[JAPSEY]:  $-5.6 \text{ kcal mol}^{-1}$  ( $-5.5, -0.1$ )

	1	2	3
1	0	-1.4	0
2	-1.4	-1.9	-0.1
3	0	-0.1	0

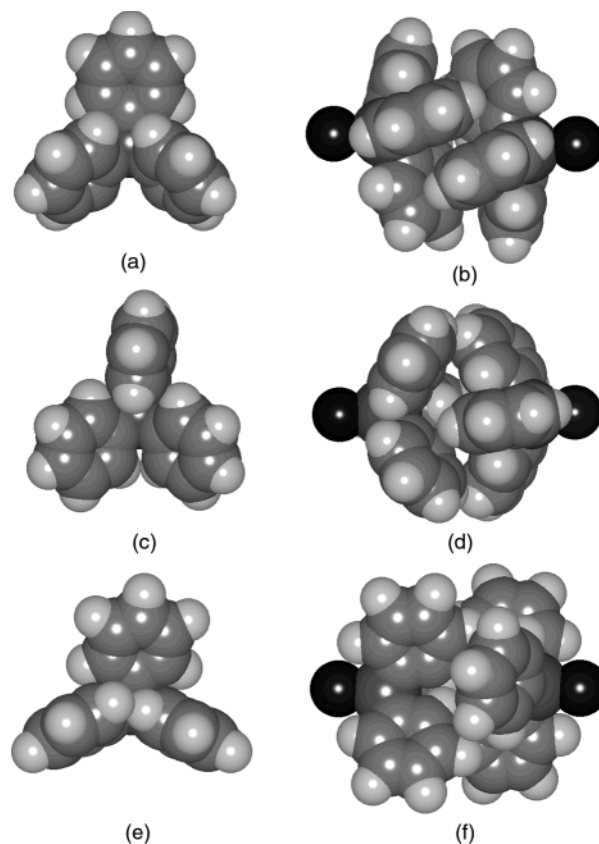


**Fig. 10** The ideal rotor (a) and the ideal 6PE (b) formed in crystalline  $(\text{Ph}_3\text{P})\text{Os}(\text{CO})_3(\text{PPh}_3)$  [COSPHP].

components of the energy for each is given in Table 1. The intermolecular energy calculated for this “ideal” embrace in [COSPHP] is  $-11.3 \text{ kcal mol}^{-1}$  for the  $(\text{PPh}_3)_2$  pair, with each of the six edge-to-face interactions contributing  $-1.6 \text{ kcal mol}^{-1}$ .

#### Variants on the sixfold phenyl embrace

As seen from the histogram above (Fig. 9), most of the  $\text{M}-\text{PPh}_3$  groups have quite a large range of torsion angles. However, the irregularity of the conformation of  $\text{M}-\text{PPh}_3$  does not mean that



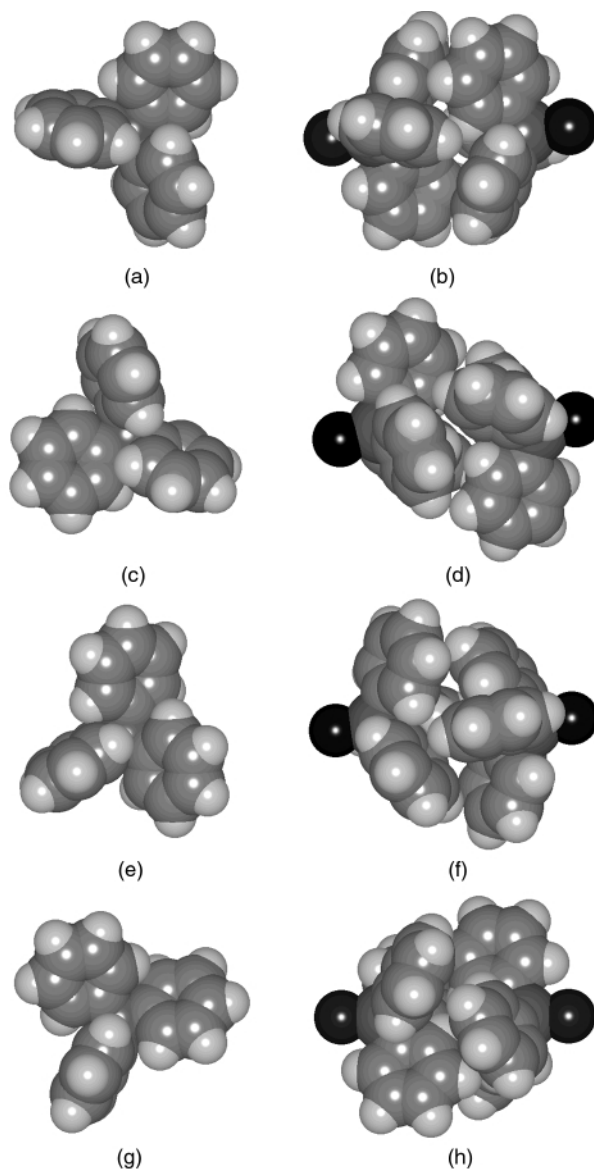
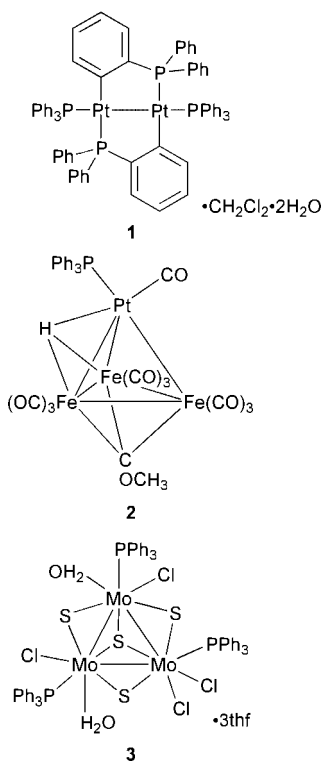
**Fig. 11** Various  $\text{PPh}_3$  flipper conformations and the 6PEs they form: (a), (b) 6PE formation from the orthogonal flipper in  $(\text{Ph}_3\text{P})_2\text{WCl}_3 \cdot (\text{NPh}) \cdot \text{toluene}$  [CAYPEX]; (c), (d) the parallel flipper in **1** [FOMDEQ]; and (e), (f) the extreme orthogonal flipper in  $[(\text{Ph}_3\text{P})_9\text{Au}_9\text{PtH}]_2(\text{NO}_3)_4 \cdot \text{Et}_2\text{O}$  [RABFIJ].

a multiple phenyl embrace is precluded. First we describe the embraces formed by each type of flipper conformation: they are 6PE in the sense that they involve six phenyl rings, but they do not have the six ef interactions.

An example of a 6PE made up of a pair of orthogonal flippers is [CAYPEX], whose torsion angles are  $-90, -35, 30^\circ$  [Fig. 11(a)]. There are four edge-to-face interactions, ranging in energy from  $-1.0$  to  $-3.3 \text{ kcal mol}^{-1}$ . Two of these are evident at the top and bottom of Fig. 11(b) which shows the 6PE. In addition, there is a very favourable offset face-to-face interaction ( $-3.0 \text{ kcal mol}^{-1}$ ) which can be clearly seen in the centre of Fig. 11(b). Crystalline **1** [FOMDEQ] shows an example of a parallel flipper taking part in a 6PE [Fig. 11(c) and (d)]. Here the  $T_i$  values are  $-61, 7$  and  $50^\circ$ . On each side of the embrace, the ring with parallel conformation is wedged into the cleft between the two mirror related rings from the other partner, forming two ef interactions which range in energy from  $-1.2$  to  $-2.0 \text{ kcal mol}^{-1}$ . Contrasting with the embrace formed by [FOMDEQ] is that found in  $[(\text{Ph}_3\text{P})_9\text{Au}_9\text{PtH}]_2(\text{NO}_3)_4 \cdot \text{Et}_2\text{O}$  [RABFIJ] [Fig. 11(e) and (f)], where the ring conformation is an extreme orthogonal flipper with  $T_i$  values of  $-1, 0$  and  $79^\circ$ . Here, there is an orthogonal ring lying over the pair of parallel rings. From Table 1, it can be seen that the interactions, which are distorted ef, each contribute from  $-1.2$  to  $-1.6 \text{ kcal mol}^{-1}$  of attractive energy.

In Fig. 12 we collect some examples of irregular  $\text{M}-\text{PPh}_3$  groups, and the multiple phenyl embraces they form.

An example of one of the more extreme variants of a rotor is  $[(\text{Ph}_3\text{P})_3\text{Au}]_2[(\text{Ph}_3\text{P})_3\text{Ag}](\text{NO}_3)_3$  [BIVRUT] where the torsion angles are  $-69, -37$  and  $-19^\circ$ . Fig. 12(a) clearly indicates the asymmetry of the rotors making up this centrosymmetric embrace which is shown in Fig. 12(b). The embrace itself is made up of two types of interaction, ef (of energy  $-1.1 \text{ kcal mol}^{-1}$ , see Table 1) and distorted off ( $-1.1 \text{ kcal mol}^{-1}$ ). One of



the former can be seen at the front of Fig. 12(b), while the latter is shown at the top.

6PE formation is also found for further assorted conformations. Groups which contain either parallel or orthogonal rings, or one of each, but are not flippers, can form multiple phenyl embraces.  $(\text{Ph}_3\text{P})_3\text{CoH}(\text{CO})$  [CAHCOP] [Fig. 12(c) and (d)] displays one orthogonal ring ( $T_i$  values of 26, 30 and  $83^\circ$ ). There are two ef interactions, one of which can be seen at the top of Fig. 12(d), which are the only well-defined individual phenyl...phenyl interactions in the embrace.  $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})(\text{COCH}_3)(\eta^5\text{-1-methyl-3-phenylcyclopentadienyl})\cdot\text{C}_6\text{H}_6$  [ACMPFE] includes one parallel ring [Fig. 12(e)] with torsion angles of  $-64$ ,  $-55$  and  $-3^\circ$ . A pair of these parallel rings takes part in an ef interaction, Fig. 12(f). [COKNAR],  $[(\text{Ph}_3\text{P})\text{Pt}(\eta^2\text{-but-2-ene})(\eta^3\text{-2-methylallyl})](\text{PF}_6)$  [Fig. 12(g) and (h)] has one parallel and one orthogonal ring ( $T_i$  values of  $-80$ ,  $-55$  and  $0^\circ$ ). This embrace includes four ef interactions, two of these can be seen at the bottom of Fig. 12(h). The parallel and orthogonal rings on the left-hand partner each take part in an ef interaction with the third ring on the other group.

#### Fourfold phenyl embraces in M-PPh<sub>3</sub>

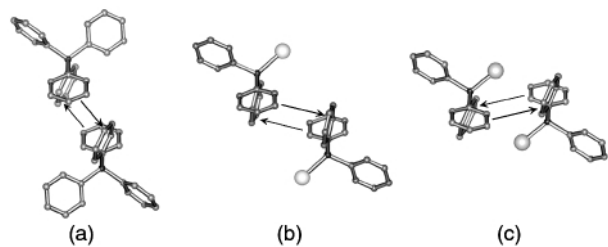
The occurrence of the fourfold phenyl embrace (4PE) in M-PPh<sub>3</sub> crystals is less than for crystals including the cation  $[\text{Ph}_4\text{P}]^+$ . There are two variants on the 4PE, orthogonal (O4PE) and parallel (P4PE). The descriptors relate to the relative orientations of the C-P-C planes for the interacting rings of the two partners.<sup>2</sup> While there are only about 200 examples of M-PPh<sub>3</sub> engaging in O4PE, there are about 1100 occurrences of P4PE in compounds containing M-PPh<sub>3</sub>. As previously defined,<sup>2</sup> there are four phenyl rings in the interaction zone of the P4PE, which take part in two edge-to-face interactions and an offset face-to-face interaction. The motif is commonly centrosymmetric, so that the two M-P vectors are parallel (but not collinear, as found for 6PE formation). For most P4PE found for  $[\text{Ph}_4\text{P}]^+$  compounds, the two C-P-C planes for the interacting rings are not only close to parallel, but also nearly coplanar [Fig. 13(a)]. For compounds of M-PPh<sub>3</sub>, these two planes are frequently far from coplanar, although parallel. The ef phenyl...phenyl interactions remain and, in some instances, the off interaction also. However, the relative orientations of the two groups

**Fig. 12** Multiple phenyl embraces formed by irregular M-PPh<sub>3</sub> groups: (a), (b) 6PE formation by  $[(\text{Ph}_3\text{P})_3\text{Au}]_2[(\text{Ph}_3\text{P})_3\text{Ag}](\text{NO}_3)_3$  [BIVRUT]; (c), (d) in  $(\text{Ph}_3\text{P})_3\text{Co}^+\text{H}(\text{CO})$  [CAHCOP]; (e), (f) in [ACMPFE],  $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})(\text{COCH}_3)(\eta^5\text{-1-methyl-3-phenylcyclopentadienyl})\cdot\text{C}_6\text{H}_6$  (g), (h) in [COKNAR],  $[(\text{Ph}_3\text{P})\text{Pt}(\eta^2\text{-but-2-ene})(\eta^3\text{-2-methylallyl})](\text{PF}_6)$ .

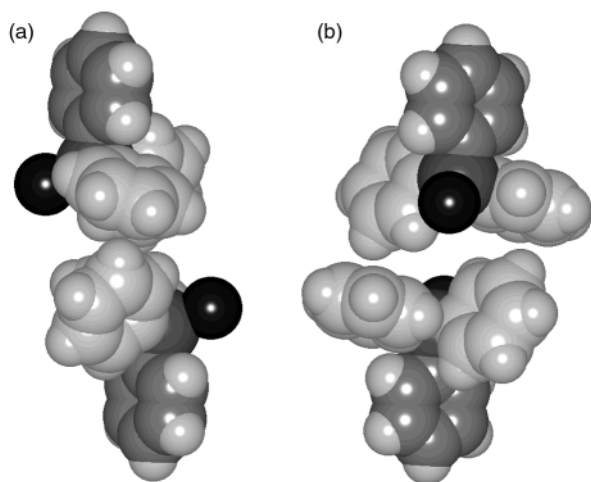
involved results in short M...M distances [Fig. 13(b)]. In the extreme, the metal atoms could be considered as being in the interaction zone, giving rise to a pseudo-6PE. This is particularly so for complexes including gold [Fig. 13(c)].

An example of the P4PE in 2 [BEBKIC] is shown in Fig. 14. The four rings forming the centrosymmetric embrace are involved in two local edge-to-face interactions, each of which contributes  $-1.6$  kcal mol<sup>-1</sup> to the intermolecular energy (see Table 1).

The two M-P-C torsion angles for the rings involved in the P4PE in Fig. 14 are approximately equal. Fig. 15 shows a scattergram of the two relevant torsional angles for M-PPh<sub>3</sub> involved in P4PE. As is evident, there is a preponderance of approximately equal (and equally signed) torsional angles. However, there is a small number of examples in the central region of Fig. 15 which represent P4PE formation by flippers. An example formed by the compound 3 [JAPSEY] is shown in Fig. 16. Here the two edge-to-face interactions, each of  $-1.4$  kcal mol<sup>-1</sup>, are accompanied by an offset face-to-face interaction with a more favourable intermolecular energy of  $-1.9$  kcal mol<sup>-1</sup> (Table 1).



**Fig. 13** (a) An edge-on view of a P4PE formed by  $[\text{PPh}_4]^+$  cations in  $[\text{S}_2\text{Mo}(\text{S})_2\text{AgCN}](\text{Ph}_4\text{P})_2$  [BUMYUD10]. The four rings in the central region are those forming the two ef interactions, which are marked with arrows. The C–P–C planes for these two rings are parallel and nearly coplanar. (b) A similar view of the P4PE formed by **2** [BEBKIC]. Note that the two C–P–C planes are still parallel, but are no longer coplanar, as the top group has shifted to the left relative to the bottom one. (c) The corresponding view for (*O*-ethylthiocarbonato-*S*)Au(PPh<sub>3</sub>) [VOPDEJ], where the shift is sufficient that the metal atoms (Au) are in the interaction zone and the two distal P–C vectors are not only parallel, but approximately collinear. This is a pseudo-6PE, where only two of the normal cycle of six ef interactions remain.



**Fig. 14** Two orthogonal views of the P4PE between molecules of **2** in [BEBKIC]. View (a) shows the antiparallel property of the P–M vectors. The embrace is centrosymmetric, with two local edge-to-face interactions, evident in view (b). The torsion angles for the rings involved are 42 and 32° (and –42 and –32°).

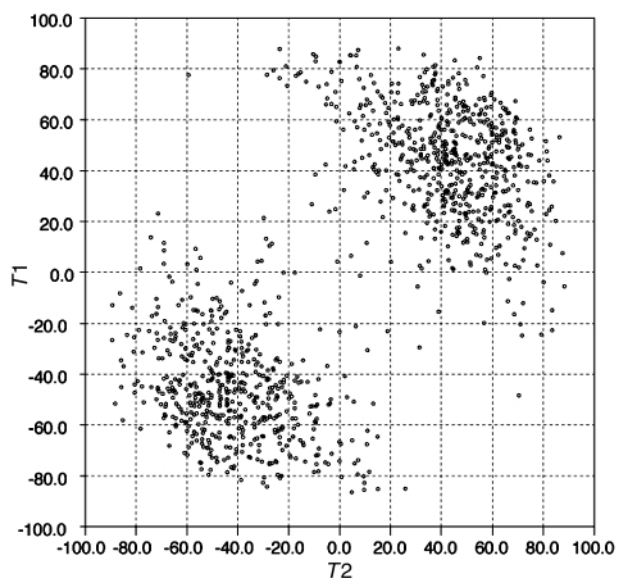
### Intermolecular energies

For supramolecular motifs, the attractive energy is the significant property. In the absence of data, we have estimated the intermolecular energies (using the summed atom–atom energy approximation) for the (PPh<sub>3</sub>)<sub>2</sub> pair in some of the embraces pictured above. Our intermolecular potential for atoms with charges  $q_i, q_j$  separated by  $d_{ij}$  is given in eqn. (1), with a distance-

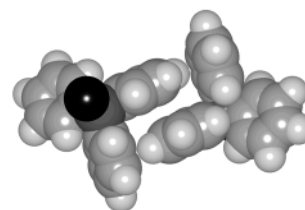
$$E_{ij} = e^a_{ij} [(d_{ij}/d^a_{ij})^{-12} - 2(d_{ij}/d^a_{ij})^{-6}] + q_i q_j / (\epsilon \cdot d_{ij}) \quad (1)$$

dependent permittivity,  $\epsilon = 1d$ . Atom charges used are: P –0.13; C<sub>ipso</sub> –0.02; C –0.08, H 0.10. The atom parameters  $e^a$  and  $d^a$  are obtained by analyses described and justified in detail in a separate paper.<sup>16</sup> The van der Waals parameters ( $e^a/\text{kcal mol}^{-1}$ ,  $r^a/\text{\AA}$ ) used for the calculations reported in this paper are: C 0.08, 1.95; H 0.02, 1.62; P 0.20, 2.10.

Table 1 contains the calculated energies for seven of the embraces already pictured. There is little difference in the energies computed for the ideal 6PE and that formed from a pair of orthogonal flippers. The first is made up of six ef interactions, while the second is comprised of four ef interactions along with an off interaction. The energies of the other 6PEs [FOMDEQ] and [RABFIJ] are less favourable, but are still comparable to the values found for less than ideal conventional 6PEs. The energies of the two different P4PEs in [BEBKIC] and [JAPSEY]



**Fig. 15** Scattergram of the pairs of torsional angles for M–PPh<sub>3</sub> groups involved in P4PE.



**Fig. 16** The P4PE formed by **3** in [JAPSEY], with torsion angles of –27 and 36°.

are less favourable again, but this would be expected since they involve only four phenyl rings. The P4PE in [JAPSEY] is more attractive, since the two ef interactions are augmented by an off interaction.

### Summary and conclusions

The majority of the very large number of characterised M–PPh<sub>3</sub> groups are not threefold rotors. There is a broad distribution of conformations of individual phenyl rings relative to the whole molecule, and wide variety in the combinations of the three M–P–C<sub>ipso</sub>–C torsional angles for each molecule. There are few combinations of these torsion angles within a ligand which would be prohibited: an obvious one is where all three rings are in the orthogonal orientation, which leads to crowding of the hydrogen atoms.

There is, however, a large proportion of M–PPh<sub>3</sub> ligands in which the ring conformations constitute a distorted rotor. We have identified the generally occurring flipper conformations, named because two rings have approximately equal and opposite torsional angles and present like a flipper. There are two subclasses of flipper, the parallel flipper and the orthogonal flipper, which are characterised by near mirror symmetry. It is the orthogonal flipper conformation which Bye *et al.* propose as the intermediate for the process of stereoisomerisation in molecules of the type Ph<sub>3</sub>PX.<sup>14</sup>

The rotor conformation and both forms of the flipper conformation of M–PPh<sub>3</sub> are capable of forming the sixfold phenyl embrace, in which all six phenyl rings participate. However, only the rotor conformation can use a concerted cycle of six local edge-to-face Ph···Ph interactions. By way of compensation, the 6PE formed by the interaction of two orthogonal flippers incorporates an offset face-to-face interaction which

gives it an intermolecular energy value comparable to that of a good conventional 6PE.

In fact, we find only 36 out of 5089 M–PPh<sub>3</sub> structures have at least one M–PPh<sub>3</sub> group with exact threefold symmetry. Twelve of these form an ideal 6PE with  $\bar{3}$  symmetry, usually in HA6PE lattices.<sup>9</sup>

We have found that M–PPh<sub>3</sub> frequently forms P4PE, but in general this embrace is different from that for [PPh<sub>4</sub>]<sup>+</sup> in that the two parallel C–P–C planes constituting the interaction zone are not coplanar. This interaction can be formed by a rotor or by a flipper, with an energy which is of the same order of magnitude as that found previously for a fourfold phenyl embrace with the coplanar arrangement.

A pair of embracing PPh<sub>3</sub> ligands has a strong supramolecular attractive energy, ranging from –11 to –5 kcal mol<sup>–1</sup> in the examples presented. These are comparable with the stronger hydrogen bonds, although it must be recognised that a multiple phenyl embrace such as this has a larger volume and number of atoms than a hydrogen bond. This does not, however, diminish the significance of the multiple phenyl embrace, which is a concerted supramolecular motif.

There can be a diversity of ligand conformations within the one structure, as in (Ph<sub>3</sub>P)<sub>3</sub>Rh(μ-CO<sub>3</sub>)Rh(PPh<sub>3</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, [CBTPRH], in space group *P* $\bar{1}$ . There are ten independent PPh<sub>3</sub> groups in the two molecules in the asymmetric unit which have the following conformations: one “ideal” rotor (all angles 20–70° and of the same sign [38, 50, 54°]), four non-ideal rotors (all angles the same sign, but one or more just outside the 20–70° range [37, 58, 75°; –73, –37, –22°; –67, –35, –16°; 16, 25, 71°]), two parallel flippers [–35, –2, 45°; –33, –3, 40°], one orthogonal flipper [–76, –3, 0°] and two unclassified ligands with torsions [–74, 0, 23°] and [–80, –49, –9°].

This assortment of ligands with varying conformations takes part in one 6PE, one 4PE and one combination where a flipper is directed towards all three rings of its partner.

In the following paper<sup>11</sup> we describe one-, two- and three-dimensional lattice networks formed in the crystal structures of M–PPh<sub>3</sub> compounds. In all these lattices, the dominant packing motif is the 6PE.

## Acknowledgements

This research is supported by the Australian Research Council.

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