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Crystal supramolecularity: sixfold phenyl embraces between PPh_3 ligands, forming extended nets in one-, two-, and three-dimensions

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The sixfold phenyl embrace (6PE) is manifest in the crystal structures of approximately 30% of the 5089 molecules with PPh_3 ligands (in the Cambridge Structural Database). This paper describes the characteristics and occurrence of the 6PE as a crystal supramolecular motif between metal complexes and clusters with PPh_3 ligands. The number of PPh_3 ligands per molecule, the coordination stereochemistry, and possible crowding of the PPh_3 ligands are included in the analysis. Molecules with multiple PPh_3 ligands can and do form one-, two-, and three-dimensional supramolecular networks constructed with these multiple phenyl embraces. We portray a representative selection of the resulting tectonic lattices based on 6PEs. Variants on the 6PE include a pseudo-embrace in which gold takes the place of a phenyl ring.

Introduction

Multiple phenyl embraces are now well established as ubiquitous attractive supramolecular motifs between molecules with XPh_2, XPh_3 and XPh_4 peripheral groups. The most frequently occurring embrace for XPh_3 and XPh_4 groups is the sixfold phenyl embrace[1,2] (6PE) in which six phenyl rings in the interaction zone participate in a concerted cycle of edge-to-face (ef) phenyl···phenyl interactions. Other common multiple phenyl embraces are the two isomers (parallel and orthogonal) of the fourfold phenyl embrace[2] (4PE). These embraces have been described in the greatest detail for crystals containing the $[Ph_4P]^+$ cation, which can engage in more than one embrace and thereby form extensive nets,[3,4] of which the zig-zag infinite chain of sixfold phenyl embraces (ZZI6PE),[5] the linear infinite chain of translational fourfold embraces (LIT4PE)[5] and the hexagonal array of sixfold phenyl embraces (HA6PE)[6–8] are the most prevalent. Anions of all sizes, shapes and charges are associated with these cation motifs, with preferences. These multiple phenyl embraces between $[Ph_4P]^+$ cations account for their widespread success in forming good crystals with diverse anions.

It is also well known in synthetic laboratories that the PPh_3 ligand endows its compounds with favourable crystallinity and often lower solubility than alkylphosphine analogues. We have previously intimated[1] the formation of 6PE by M–PPh_3 groups. In the preceding paper,[9] we have investigated this further, and analysed the geometry of coordinated PPh_3 in relation to its ability and propensity to form the 6PE. Somewhat surprisingly, the expected rotor geometry for M–PPh_3 with approximate threefold symmetry occurs in only about 40% of the more than 8600 M–PPh_3 groups in the Cambridge Structural Database (CSD). There are other intramolecular conformations for M–PPh_3 including the parallel and orthogonal flipper,[9] which do not have rotor geometry around the M–P axis.

Despite the substantial intramolecular variability of the M–PPh_3 group, it can and does still form multiple phenyl embraces, which include symmetrical 6PEs, distorted 6PEs, and parallel fourfold phenyl embraces (P4PEs). The calculated energies for the various embraces are quite strongly attractive, in the range −5 to −11 kcal mol^{-1}.[9]

We have also described some of the higher order multiple phenyl embraces (such as 8PE and 12PE) which have been found to occur in compounds of the type $[M(PPh_3)_x]$ where $x = 3$ or 4.[10] A higher order embrace is one where the interaction between the two molecules is not restricted to one PPh_3 ligand on each. Instead, there is involvement of more than one PPh_3 ligand in the molecule and so more than six phenyl rings are involved.

In this paper we report a search of the CSD to investigate the extent to which multiple phenyl embraces involving PPh_3 ligands can function as extended supramolecular motifs. In particular we examine: (a) the number of compounds containing different numbers of PPh_3 ligands and any influential intramolecular interactions between them, (b) the extent of 6PE formation, and (c) tectonic supramolecular networks built from embracing PPh_3 ligands. We will describe one-, two-, and three-dimensional networks of these embraces, some of which are highly symmetric. Our objective is to develop a better understanding of the various contributors to the crystal packing of compounds with PPh_3 ligands.

Results

There are 5089 compounds in the Cambridge Structural Database[11,12] (CSD v5.17a, April 1999; entries with coordinates) containing M–PPh_3. In 4438 of these there is an intermolecular P···P distance < 9 Å, indicating some form of interpenetration of the ligands.

The conformations of M–PPh_3 are described in terms of the three M–P–C_{ipso}–C torsional angles, T_i, selected to be in the range −90 to +90°.[9] Conformations where all three torsion angles have the same sign and lie within the range 20–70° are called rotors, and are about 40% of the total. Symmetric rotors, where $T_2 - T_1$ and $T_3 - T_2$ (for increasing T_i) are both in the range 0–20°, occur in only about 25% of M–PPh_3 groups. There are conformations where one torsion angle is near 0 or 90° and the other two are $\pm x°$, which are the parallel flipper and the orthogonal flipper, respectively. The occurrence of "ideal" examples of flippers, where $T_2 + T_3 < 10°$ is quite low, with only 111 examples of orthogonal flippers ($80 < T_1 < 90°$) and 22 of parallel flippers ($0 < T_1 < 10°$). Many of the remaining M–PPh_3

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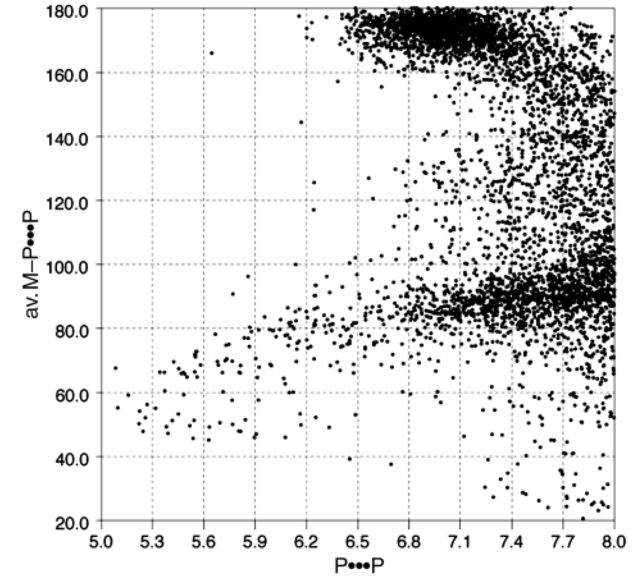

Fig. 1 Scattergram of the geometrical properties of intermolecular contacts in crystals between $MPPh_3$ functions. The ordinate is the average of the two M–P · · · P angles for each P · · · P distance.

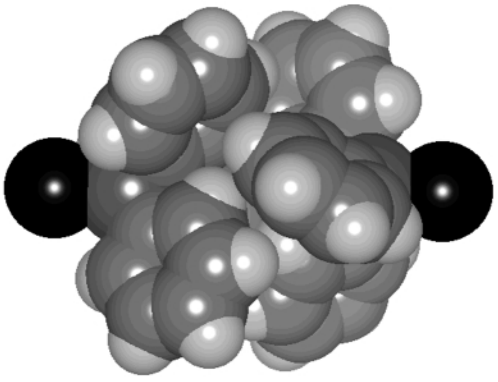

Fig. 2 An ideal 6PE with threefold symmetry, formed between two molecules of $(Ph_3PPd)_8As_6Pd\cdot3thf$ [CSD refcode VEDZOT]. Hydrogen atoms omitted.

groups can be described as deviations from one of these conformations.

Fig. 1 shows a plot of intermolecular P · · · P distances *vs.* the average of the two M–P · · · P angles for intermolecular $M–PPh_3 \cdots Ph_3P–M$ pairs. It shows a preponderance of interactions in the domain 6.5 Å < P · · · P < 7.5 Å, 160° < M–P · · · P ≤ 180°, which are 6PEs.†

We have found that 6PE formation is possible not only with rotors, but also with flippers. 6PEs constructed from $M–PPh_3$ groups in each of the two flipper conformations have been illustrated in the preceding paper.[9] An important feature of a 6PE is that there is inversion symmetry (real or pseudo) at its midpoint. So, while the torsion angles in a particular ligand might not be ideal for the 6PE, there can be a corresponding variation in the angles of its partner. This point will be illustrated in some of the examples given below.

An ideal rotor 6PE has three-fold symmetry (as occurs in the HA6PE lattice)[6,7] and is illustrated in Fig. 2, where the three M–P–C–C torsion angles are 37.7°.

In the following, we describe the occurrence of 6PE motifs in crystals of compounds with PPh_3 ligands, and also significant intramolecular interactions for molecules crowded with PPh_3 ligands. These are organised according to increasing number of PPh_3 ligands per molecule, and build up to elaborate supramolecular networks constructed from the 6PE motif. We present selected examples of the main features.

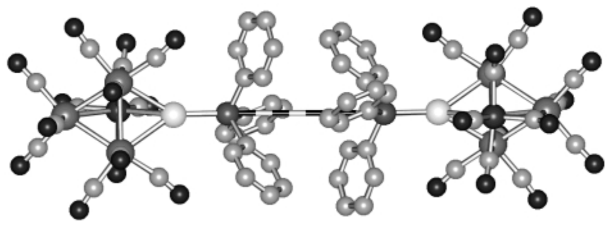

Fig. 3 $(Ph_3P)AuCoRu_3(CO)_{13}$ [CEJDOK] which forms dimeric units linked by a 6PE. Hydrogen atoms omitted. The striped lines indicate the 6PE.

Molecules with a single PPh_3 ligand

There are about 2000 examples of molecules containing a single PPh_3 ligand, of which approximately 25% form a 6PE in their crystal lattices. One of these is $(Ph_3P)AuCoRu_3(CO)_{13}$ [CEJDOK], Fig. 3. In this example, the torsion angles for the three phenyl rings of one molecule are 29, 41, 65° (and those for the centrosymmetrically related partner are −29, −41 and −65°). Although there is variation in the torsion angles, a good 6PE is still formed. These 6PE pairs interact further using one phenyl ring from one molecule and two from the other to form infinite chains of interactions in a direction roughly orthogonal to the 6PE axis, with P · · · P = 9.35 Å.

Molecules with two PPh_3 ligands

In the CSD, there are about 2200 compounds with two PPh_3 ligands per molecule. The ligands can be coordinated to a single metal atom, or to a metal cluster core. About 30% of these compounds form 6PEs in their crystal lattices. Of those forming 6PEs, about half form one such embrace and half form two.

The stereochemistry at the metal centre in these compounds can be trigonal, tetrahedral, square planar or octahedral, affecting the angle between the two M–P vectors. The *trans* configuration of the two PPh_3 ligands for a square planar or octahedral stereochemistry at the metal centre negates the possibility of intramolecular interactions between PPh_3 ligands and when both form 6PEs, the extended supramolecular motif is the linear chain. This is a very common motif. An example of a molecule with a single metal core forming such a linear chain is $(Ph_3P)Ir(CO)(OH)(PPh_3)$ [BOMROK], Fig. 4.

When the two PPh_3 ligands are adjacent and close, as in the case of trigonal, tetrahedral or *cis* square planar, or octahedral metal stereochemistry, the phenyl rings are capable of intramolecular (but interligand) interactions. The type and extent of such interactions depend on the P–M–P angle. When this angle is *ca.* 100° a single offset face-to-face pair is the only intramolecular interaction. However, as the P–M–P angle increases, it is possible for the rings to be oriented so as to accommodate a pair of intramolecular edge-to-face interactions. These two types of intramolecular interligand interactions are shown in Fig. 5: they represent the ideals and there are other possibilities.

If both the PPh_3 ligands in these compounds with *cis* P–M–P angles take part in 6PEs, the resulting infinite chain is a zig-zag, as in Fig. 6. An example is $(Ph_3P)_2Cu(Cl)(dithiooxamide)$ [DAVDAF] which has zig-zag infinite chains of centrosymmetric 6PEs (P · · · P = 6.89, 7.31 Å, alternating along the chain).

Molecules with three PPh_3 ligands

When three PPh_3 ligands are attached to a metal cluster core, the extent of intramolecular interactions between the ligands

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† For $[Ph_4P]^+$ cations, our geometric criteria for defining a 6PE are that P · · · P < 7.0 Å and that both C_{distal}–P · · · P angles lie in the range 160–180°.

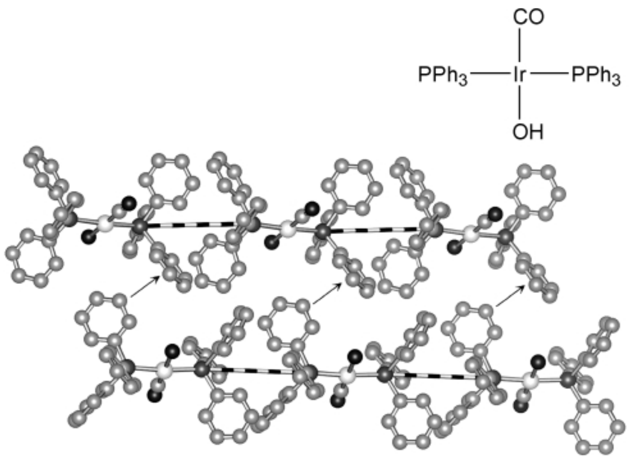

Fig. 4 $(Ph_3P)Ir(CO)(OH)(PPh_3)$ [BOMROK] with linear infinite chains of 6PEs (P···P = 7.06 Å). The torsion angles describing the orientations of the phenyl rings participating in the non-centrosymmetric 6PE are 34, 42, 66° and −34, −49, −60°. There are edge-to-face phenyl···phenyl interactions between chains (P···P 8.5 Å) which link the chains into layers and these are indicated by the arrows.

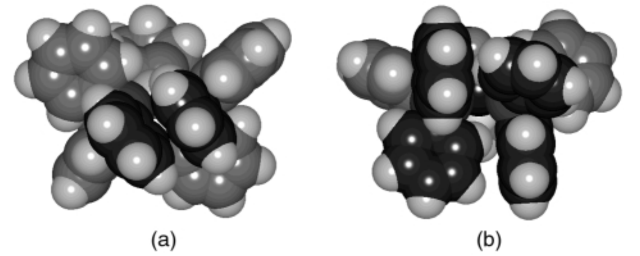
(a) (b)

Fig. 5 Examples of $M(PPh_3)_2$ groups showing the intramolecular interactions which might occur when the P–M–P angle is (a) *ca.* 100° and (b) *ca.* 125°. In (a) there is a single offset face-to-face intramolecular phenyl···phenyl interaction, while in (b) there is a pair of edge-to-face interactions. The interacting rings are shaded darker for emphasis.

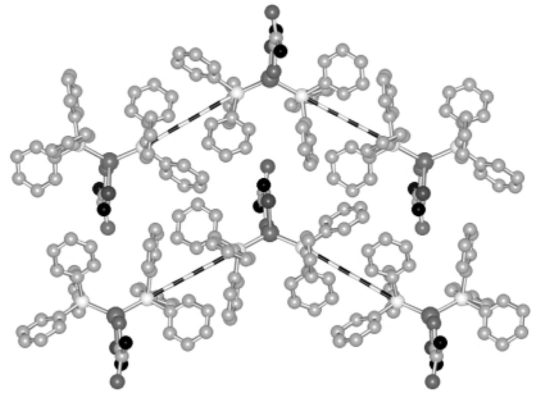

Fig. 6 A zig-zag chain formed when two PPh_3 ligands in *cis* configuration each take part in a 6PE. $(Ph_3P)_2Cu(Cl)(dithiooxamide)$ [DAVDAF] forms such an infinite chain of centrosymmetric 6PE (P···P = 6.89, 7.31 Å, alternating along the chain).

depends on the size of the core. When the three ligands all coordinate to a single metal atom the coordination stereochemistry can be trigonal planar {*e.g.* $[Ni(PPh_3)_3]^0$ [JEKCIL]}, tetrahedral {*e.g.* $Co(OPh)(PPh_3)_3$ [DILTAT]}, trigonal pyramidal {*e.g.* $AuCl(PPh_3)_3$ [BOJJEP]}, trigonal bipyramidal {*e.g.* $Co(CO)H(PPh_3)_3$ [CAHCOP]}, square planar {*e.g.* $RhH(PPh_3)_3$ [DOSRUY]} or octahedral {*e.g.* $ReF(CO)(NO)(PPh_3)_3$ [BONRAX]}. These molecules have interactions between the phenyl rings of adjacent ligands. In the case of the square planar metal centre, there can be two offset face-to-face sets of phenyl rings [see Fig. 7(a)]. When the metal centre displays pseudo-threefold symmetry, frequently there is formation of a threefold cycle of axially directed rings each taking part in two edge-to-face interactions. We have previously reported[10] that $[Pd(PPh_3)_3]^0$ crystallises with this threefold cycle on one side of the molecule, accompanied by a triplet of pairs of offset face-to-face interacting rings on the other side [see Fig. 7(b)]. It is this triplet of interacting phenyl rings which form a 12PE when a second molecule abuts.[10] When the core is larger than a single metal atom, there is still scope for intramolecular interactions but these are more varied and less attractive.

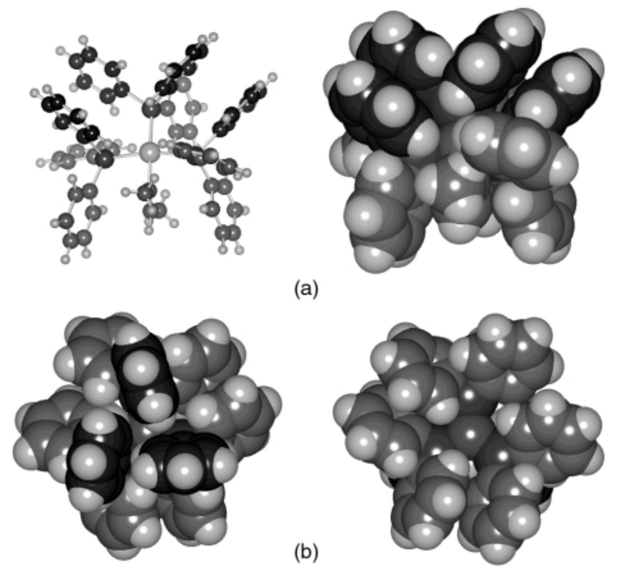
(a)
(b)

Fig. 7 (a) Skeletal and space-filling representations of the two pairs of offset face-to-face interactions between PPh_3 ligands in $[(Ph_3P)_3Pt(trans\text{-}2\text{-butenyl})](F_3CSO_3)\cdot 0.5CH_2Cl_2$ [JANFOT] with a square planar metal centre. (b) Threefold intramolecular interligand interactions in $[Pd(PPh_3)_3]^0$ [VACKEP]. A triplet of edge-to-face interactions occurs on one side, and three pairs of face-to-face interaction occur on the other.

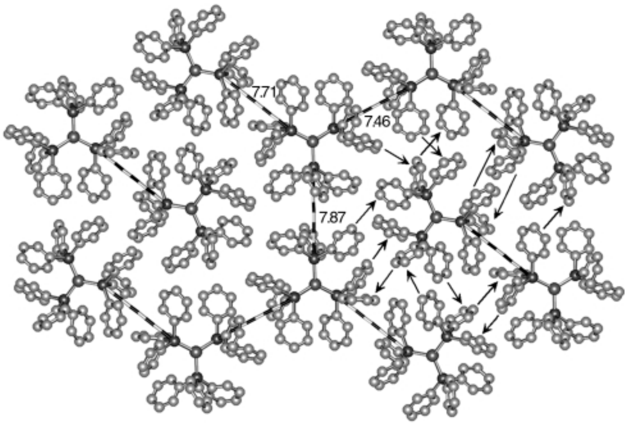

Fig. 8 Part of the crystal lattice of $Ni(PPh_3)_3$ [JEKCIL] showing the quasi hexagonal array of complexes. There are two independent molecules in the asymmetric unit—one of them takes part in three 6PE with P···P distances of 7.46, 7.71 and 7.87 Å (note that two of these distances lie outside the criteria used for the statistics above). The second independent molecule, which is located at the centre of the hexagon only takes part in the 6PE with a P···P distance of 7.71 Å. There are further interactions between this molecule and those comprising the hexagonal net, which are denoted by arrows on the right hand portion of the figure. The array is very nearly planar and there are additional interactions between the layers.

Of the 300 molecules with three PPh_3 ligands, 72 form only one 6PE as a supramolecular pair, while 22 form two 6PEs in chains which are linear or zig-zag. $[Ni(PPh_3)_3]^0$ [JEKCIL] with trigonal planar stereochemistry at Ni forms a nearly hexagonal array of molecules linked by 6PEs (but not all of optimum geometry), as detailed in Fig. 8.

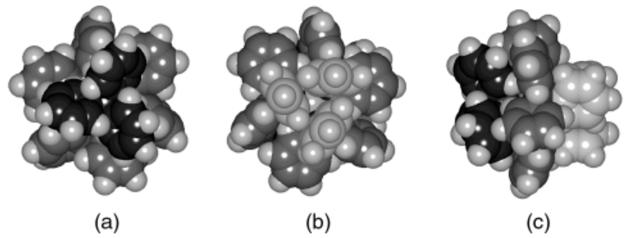

Fig. 9 Intramolecular interactions for a tetrahedral molecule of the type $[M(PPh_3)_4]^+$. (a) Three rings from a single PPh_3 ligand, along a threefold axis of the molecule. (b) Three rings from different PPh_3 ligands on the side of the molecule opposing that in (a): note the triplet of edge-to-face interactions. (c) A side view of the molecule with the threefold axis horizontal, with both sets of rings evident and differentiated by their shading, along with the central girdle of interacting rings.

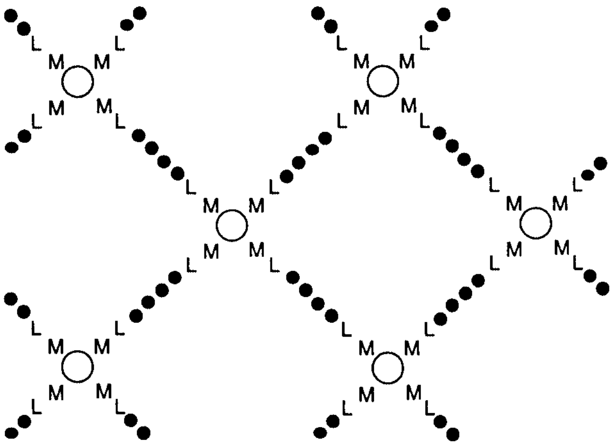

Fig. 10 Square planar array of four 6PEs around a metal cluster.

Molecules with four PPh_3 ligands

There is a group of compounds containing $[M(PPh_3)_4]^+$, which we have examined previously.[10] These compounds all have tetrahedral M and real (or pseudo) T_d symmetry. Each face of the tetrahedron exhibits the threefold cycle of edge-to-face interacting phenyl rings noted in Fig. 7(b) above for $M(PPh_3)_3$ centres. Opposite the threefold cycle is a PPh_3 ligand. If these two arrays approach intermolecularly, the motif formed is that previously described as a hybrid 6PE (or H6PE) where three of the embracing rings come from a single ligand, while the other three originate from three different ligands. Around the girdle of the molecule, six phenyl rings alternate in their orientation so that there is a sixfold cyclic edge-to-face array. Because of the T_d symmetry of the molecule, there are four such girdles. Unlike all the other interactions described in this paper, pairs of adjacent phenyl rings around the girdle are part of the *same* PPh_3 ligand. The various aspects of the intramolecular phenyl···phenyl interactions in $[M(PPh_3)_4]^+$ are shown in Fig. 9. Most of these compounds do not form 6PEs, but have been found to form higher order embraces instead, presumably because of the high density of phenyl rings and their inflexibility of location on the surface of the molecule.

When the four PPh_3 ligands are coordinated to a metal cluster and therefore not constrained by intramolecular interactions, it is possible for all four ligands to form 6PEs. The crystal lattice array resulting from formation of four 6PEs depends on their relative dispositions. If the four M–P bonds are coplanar and arrayed approximately orthogonally around the central core of metal atoms, then a layer of 6PEs occurs (Fig. 10). Often the molecular symmetry is twofold rotation or inversion, and the layer can be flat or puckered. An example of a (crystallographically) planar layer occurs in $Cl_3Sn(AuPPh_3)_4SnCl_3$ [LECMAH], Fig. 11.

As an alternative to the extended 6PE motifs of Figs. 10 and 11, the four M–P vectors can be coplanar, but approximately parallel to each other. This leads to a double stranded array (see Fig. 12). Examples of this double stranded motif occur in $Ag_{14}(SBu^t)_8(PPh_3)_4{\cdot}CHCl_3$ [CAYZOR], shown in Fig. 13, and $(OC)(Ph_3P)_2Ir(\mu\text{-tetracyanoethylene})Ir(PPh_3)_2(CO){\cdot}CH_3CN$ [SUGTUJ].

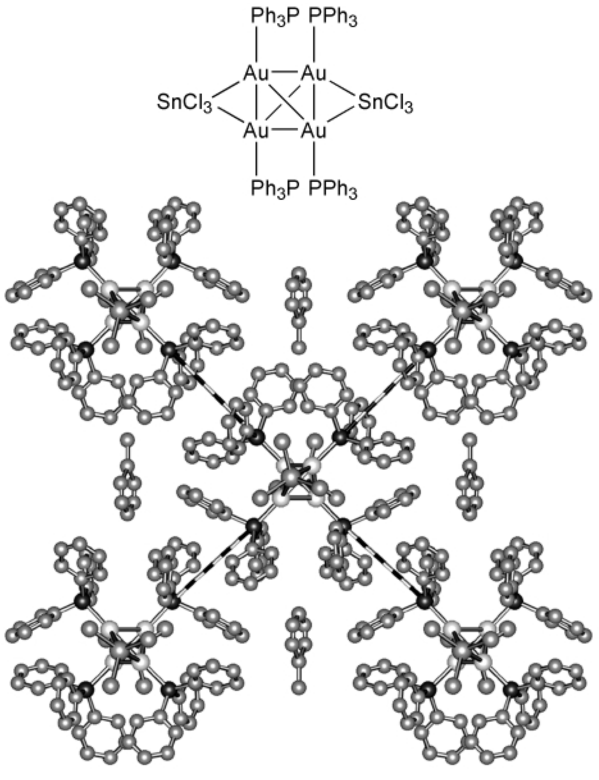

Fig. 11 The square array of 6PEs formed by $Cl_3Sn(AuPPh_3)_4SnCl_3$ [LECMAH]. Note the inclusion of the solvent toluene which is in a position suitable for formation of several edge-to-face interactions.

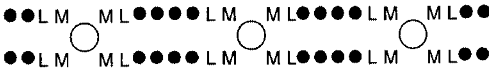

Fig. 12 Diagrammatic representaion of the double stranded chain motif formed when parallel pairs of PPh_3 ligands protrude from the metal core.

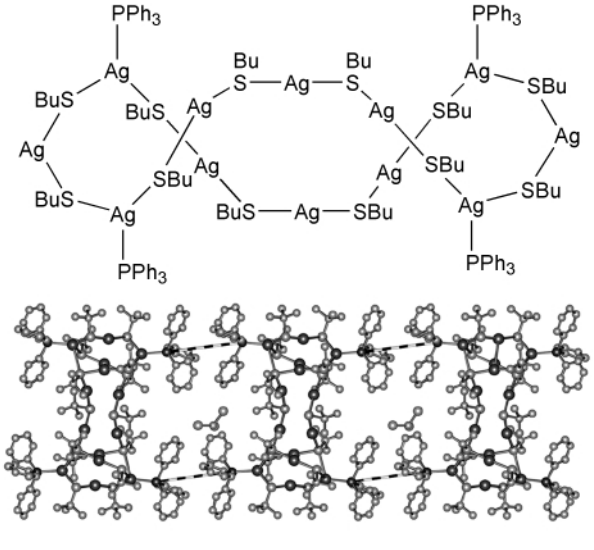

Fig 13 The double stranded chain formed by $Ag_{14}(S\text{–}Bu^t)_8(PPh_3)_4{\cdot}CHCl_3$ [CAYZOR]. The $CHCl_3$ solvent occupies the cavities along the strand and takes part in C–H···Cl interactions.

Finally, if the four M–P vectors are arrayed tetrahedrally about a metal cluster core, but not a single metal atom, a diamondoid supramolecular lattice can be formed. The only

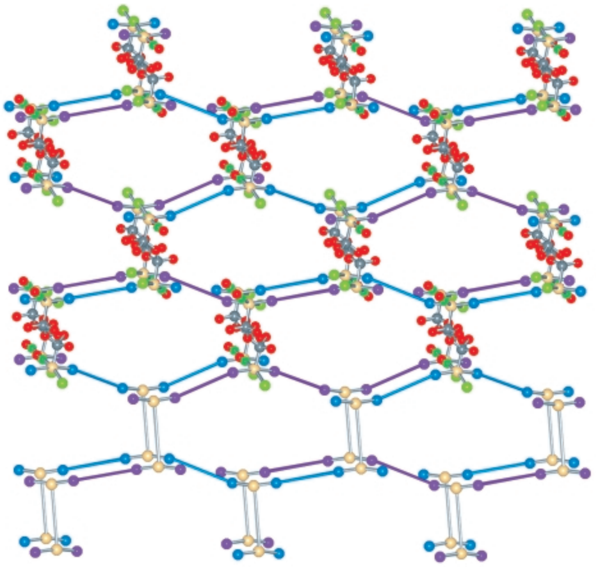

Fig. 14 The diamondoid array formed by $(Ph_3P)_2(Cl)(CO)Os\{Si(OH)_2O(OH)_2Si\}Os(CO)(Cl)(PPh_3)_2$ [LADDEZ]. The two interpenetrating lattices in the crystal structure are differentiated by the colouring of the rods representing the 6PE. The phenyl rings have been omitted. In the lower part of the diagram, the central portion of the molecule has been replaced by solid lines for further clarification.

example we have found in the CSD of a tetrahedral array of 6PE occurs in $(Ph_3P)_2(Cl)(CO)Os\{Si(OH)_2O(OH)_2Si\}Os(CO)(Cl)(PPh_3)_2$ [LADDEZ], shown in Fig. 14. The central portion of the molecule is extended and its array of four PPh_3 ligands is far from ideally tetrahedral, resulting in a distortion of the diamondoid lattice. A single diamondoid lattice would result in too much empty space in the crystal structure, so in this case, two interpenetrating diamondoid lattices result. This is shown in Fig. 14 where the rods representing the 6PE in the two lattices are distinguished by their colour. There are no significant phenyl···phenyl interactions between the two nets.

Interpenetrating lattices have been reviewed recently.[13] In most cases, the lattice connectors are held together by conventional covalent bonding, but there are supramolecular examples in which the connectors are O–H···O hydrogen bonding. The crystal LADDEZ is the only example we know of where the connectors are multiple phenyl embraces.

Molecules with more than four PPh_3 ligands

There are 148 molecules in the CSD which contain five or more PPh_3 ligands. The distribution is: 32 with five PPh_3 ligands, 58 with six PPh_3 ligands, 21 with seven PPh_3 ligands, 31 with eight PPh_3 ligands, one molecule with nine PPh_3 ligands, and five molecules with ten PPh_3 ligands. The size of the metal core compared with the number of PPh_3 ligands surrounding it determines whether there are favourable intramolecular interactions between the ligand rings. With a large number of PPh_3 ligands, there is scope for more complex nets of 6PE. There are several examples where each molecule contains eight PPh_3 ligands and each ligand takes part in a 6PE, to form a body-centred cubic array around each molecule. Examples include $(Ph_3PPd)_8As_6Pd·3thf$ [VEDZOT], Fig. 15, $[\{(Ph_3P)_2Pt\}_2S_2PdS_2\{Pt(PPh_3)_2\}_2](BF_4)_2$ [CAJMOP], Fig. 16, and $[\{(Ph_3P)_2ReH_6\}_4Cu_6]^{2+}(PF_6)^-(OH)^-·2CH_3CN$ [YADLIY].

Partially non-molecular compounds linked by 6PE

There are five examples of one-dimensionally non-molecular compounds which associate to form layers by the formation of 6PE linkages. One such example is $[(\mu\text{-}NO_3)Hg(PPh_3)(NO_3)]_\infty$ [NITPHG] which is shown in Fig. 17.

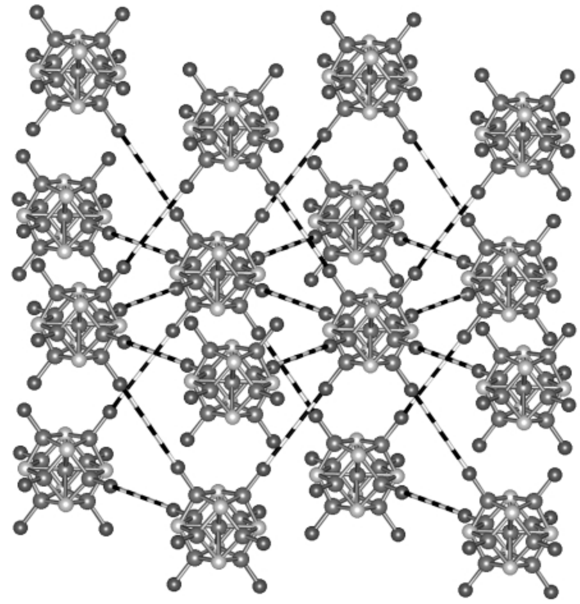

Fig. 15 $(Ph_3PPd)_8As_6Pd·3thf$ [VEDZOT] showing the high symmetry array of 6PEs. The phenyl rings of the ligands have been omitted for clarity.

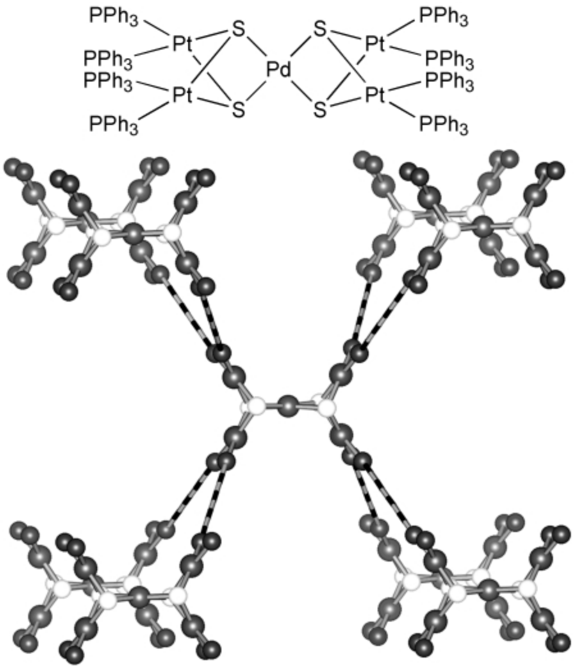

Fig. 16 $[\{(Ph_3P)_2Pt\}_2S_2PdS_2\{Pt(PPh_3)_2\}_2](BF_4)_2$ [CAJMOP] illustrating the formation of eight 6PEs by each molecule. Only the metal cluster core and the P atoms have been included.

Propagation by combination of the 6PE with other embraces

In the preceding paper,[9] we described the distorted parallel fourfold phenyl embrace (P4PE) for M–PPh_3 compounds, where there is a relative shift of the two partners so that the two C–P–C planes of the four participating rings, though parallel, are not coplanar, as they are in the analogous embrace in $[Ph_4P]^+$ complexes. The P–M bonds are antiparallel, but not collinear, with $P\cdots P < 8.0$ Å. The four rings in the interaction zone take part in two ef interactions with the possibility of an off interaction also. This motif is often centrosymmetric. The parameters which define this embrace are $P\cdots P < 8.0$ Å, and both M–P···P angles around 90°. In the scattergram of Fig. 1 these parameters account for the dense swathe of points in the central region. An example of this embrace is shown in Fig. 18, for the structure $[\{Fe(CO)_3\}_3COCH_3]HPt(CO)(PPh_3)$

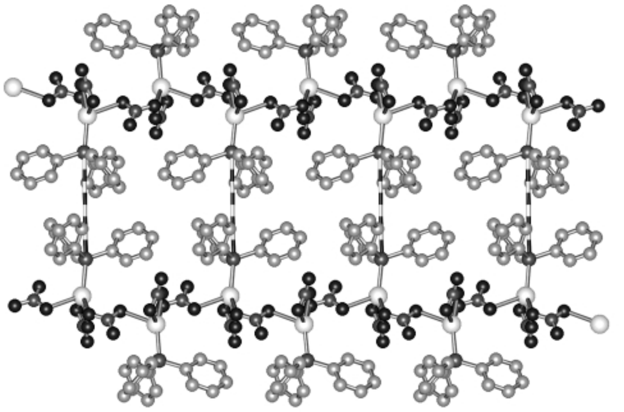

Fig. 17 The layer formed when one dimensionally infinite $[(\mu\text{-}NO_3)Hg(PPh_3)(NO_3)]_\infty$ [NITPHG] is linked by 6PEs.

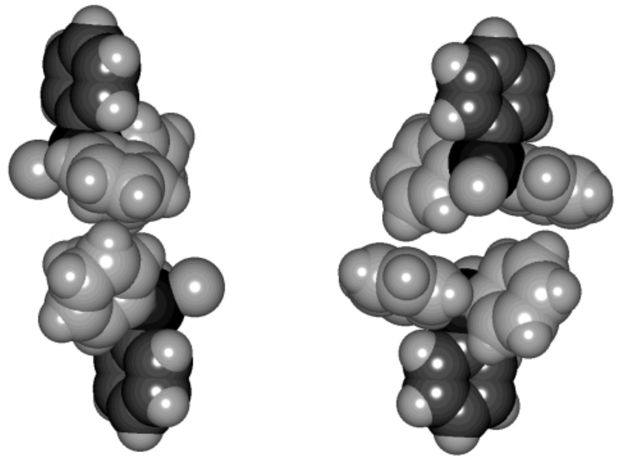

Fig. 18 Space filling representation of a P4PE formed by [BEBKIC]. The antiparallel nature of the two M–P vectors can be seen from (a), as can the location of the uninvolved phenyl rings. In (b), the edge-to-face interactions between the two pairs of rings can be seen.

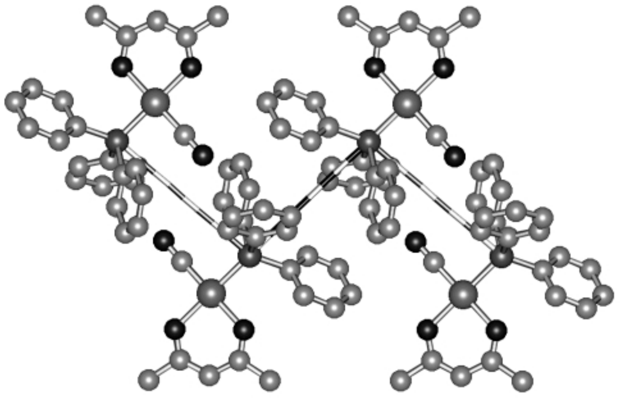

Fig. 19 The zig-zag chain formed in $(PPh_3)Rh$(acetylacetonato)(CO) [ACRHCP] propagated by alternate 6PEs (centre) and P4PEs (on each end). The CO group also interacts with the phenyl rings surrounding it.

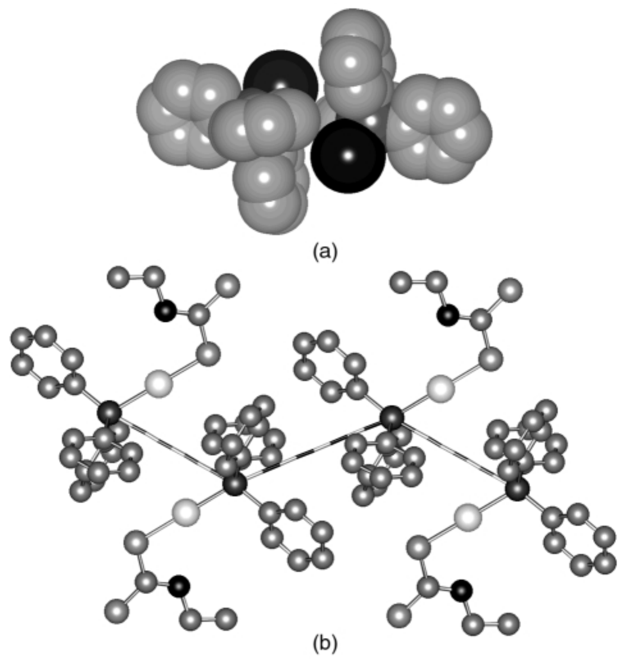

Fig. 20 (a) The LP4PE, or pseudo-6PE, found in [VOPDEJ]. The colinearity of the uninvolved phenyl rings is evident. (b) A zig-zag chain of molecules in [VOPDEJ], participating in alternating 6PEs and pseudo-6PEs.

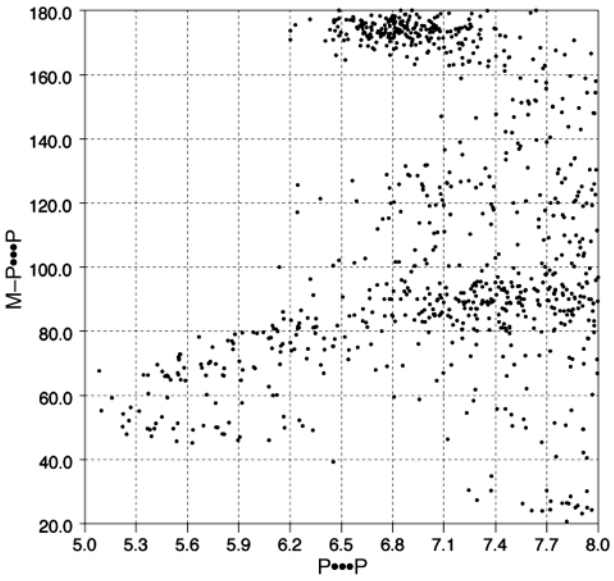

Fig. 21 Scattergram of the geometrical properties of intermolecular contacts in crystals containing $AuPPh_3$. Note the preponderance of points with $P\cdots P < 6$ Å and Au–$P\cdots P$ around 60°.

[BEBKIC]. It has been found that this motif can be combined with a 6PE to form a chain, analogous to the frequently observed ZZI6PE chain formed by $[Ph_4P]^+$ cations. An example of this is shown in Fig. 19 where the 6PE and P4PE motifs alternate.

An interesting variant of the 6PE was found when investigating those structures where the $P\cdots P$ distances are shortest. Almost without exception, these structures arise in gold complexes and a closer inspection reveals that, in these embraces, the two phenyl rings which are not involved in the embrace have nearly parallel and collinear P–C vectors. This is the same arrangement that is found in the 6PE for structures containing $[Ph_4P]^+$. In other words, for these gold compounds, the P4PE can be described as a 6PE in which two of the phenyl rings have been replaced by Au atoms—a pseudo-6PE. An example of this pseudo-6PE is given in Fig. 20(a) for $(Ph_3P)AuS(CS)OEt$ [VOPDEJ]. In many of these simple Au structures, chains of molecules form, analogous to the previously described ZZI6PE,[5] but in these chains, there are alternating 6PEs and pseudo-6PEs. Part of a chain is shown in Fig. 20(b).

The geometric parameters for this Au pseudo-6PE are $P\cdots P < 8.0$ Å and the M–$P\cdots P$ angles both around 60°. The scattergram shown in Fig. 21 is analogous to that in Fig. 1, except that it is confined to structures containing Au–PPh_3. There are many points indicative of a 6PE (Au–$P\cdots P$ angles

Table 1 Distribution of PPh_3 ligands on molecules in the Cambridge Structural Database, and the occurrence of 6PE motifs between them

		Number of PPh_3 ligands			
	Total	1	2	3	4
Number of crystal structures	5089	2058	2169	302	258
Number forming at least one 6PE	1523	504	703	94	107
			385 form 1	72 form 1	30 form 1
			318 form 2	22 form 2	53 form 2
				0 form 3	5 form 3
					19 form 4

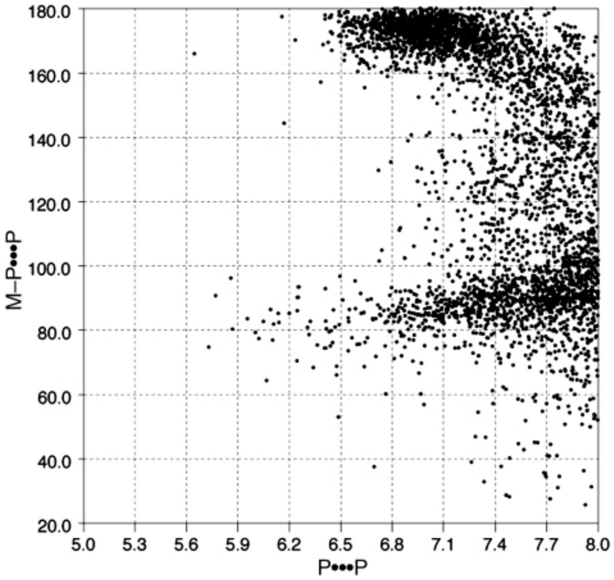

Fig. 22 Scattergram of the geometrical properties of intermolecular contacts in crystals containing $MPPh_3$, but omitting those where M = Au.

both in the range 160–180°), but there are also many points indicating very short P···P distances (< 6 Å) and angles around 60°—a pseudo-6PE. In fact, virtually all points in Fig. 1 in this region are attributable to Au complexes. This can be seen by Fig. 22, where the structures including a Au–PPh_3 moiety have been omitted.

The occurrence of pseudo ZZI6PE chains is becoming more apparent the more we delve into this area of supramolecular chemistry. We have now identified examples where the group replacing the phenyl ring is –CH_3, –Cl,[14] –S of an S_n chain,[15,16] –O of Ph_3PO [*e.g.* HAPYUS] and here, –Au.

Statistical summary

There are 5089 crystal structures in the CSD (v5.17a, April 1999) containing at least one PPh_3 ligand. The numbers of PPh_3 ligands per molecule, and the occurrence of the 6PE in these structures, are outlined in Table 1.

PPh_3 compounds which do not form 6PEs or other embraces

The 70% of structures containing M–PPh_3 which do not form a 6PE cover a diverse range of compounds, both in chemical type and size. Many of them contain other aryl groups which could compete for aryl···aryl interactions. A sizeable proportion are carbonyl compounds. These compounds could be described as having two distinct ends—a highly phenylated and a CO-rich end. A cursory inspection of this group of compounds indicates some preference for the phenylated regions of the molecule to pack adjacent to CO groups. It is possible that there are attractive interactions (such as C–H···O) occurring here, which are competing with the phenyl embraces which might otherwise be formed.

Conclusions and summary

The 6PE is a common motif occurring in the crystal structures of many of the large class of compounds incorporating the PPh_3 ligand. There can be single or multiple occurrences of this motif between molecules and, in many instances, it is the motif which controls the complete crystal structure. We have found that the intramolecular energy associated with the 6PE in these compounds is more favourable than that found for complexes including the $[Ph_4P]^+$ cation, which also frequently forms this motif. The attractive energy of a good 6PE between PPh_3 ligands is of the order of 12 kcal mol^{-1}, while that between $[PPh_4]^+$ cations is about half this. Although the van der Waals components of energies of the two interactions are similar, the electrostatic component is different. For a 6PE between PPh_3 ligands, the electrostatic component is small, typically less than 1 kcal mol^{-1}, but for the intercation embrace, the electrostatic contribution to the total energy is significant (up to 6 kcal mol^{-1}) and repulsive.

The frequency of occurrence of 6PEs in metal complexes with PPh_3 ligands is less than that for crystals containing $[Ph_4P]^+$. This is probably accounted for by the fact that the $[Ph_4P]^+$ cation forms only multiple phenyl embraces, and frequently forms chains or nets in which each $[Ph_4P]^+$ is involved in two or three embraces, while the metal complexes have functionalities other than PPh_3 and can form competing intermolecular interactions.

We have found several classes of supramolecular networks for complexes of the PPh_3 ligand which are engineered by the 6PE motif. The most frequently occurring is the linear chain, which occurs in complexes with two *trans* PPh_3 ligands. Planar arrays are also common for complexes with four planar, orthogonal PPh_3 ligands coordinated to a metal cluster centre. Finally, we have presented several examples of three dimensional arrays formed by highly symmetrical complexes with eight PPh_3 ligands, and non-molecular compounds which link into layers by multiple 6PEs. Our coverage of elaborate supramolecular nets based on the 6PE between PPh_3 ligands has not been comprehensive, but representational. Examination of the crystal packing for symmetrical $(M\text{–}PPh_3)_n$ molecules, or those in high symmetry space-groups, often reveals such networks.

Acknowledgements

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