Crystal supramolecularity: elaborate six-, eight- and twelve-fold concerted phenyl embraces in compounds $[M(PPh_3)_3]^z$ and $[M(PPh_3)_4]^z$†

Ian Dance* and Marcia Scudder

School of Chemistry, University of New South Wales, Sydney 2052, Australia

Multiple phenyl embraces are concerted supramolecular motifs based on intermolecular phenyl–phenyl attractions, mainly in the edge-to-face (**ef**) geometry. Variations of the six-fold phenyl embrace (6PE) and higher order multiple phenyl embraces involving eight or twelve phenyl groups are described. They occur in crystals of metal complexes with three or four Ph_3 ligands. The enlarged 6PE (E6PE) involves phenyl groups from three Ph_3X ligands in each of two molecules, and is formulated generally as $(XPh)_3\cdots(PhX)_3$: the H6PE, or $(XPh)_3\cdots(Ph_3X)$, is a hybrid of the E6PE and the 6PE [which is $(XPh_3)\cdots(Ph_3X)$]. The 8PE uses $\{M(XPh_2)_2\}\cdots\{(Ph_2X)_2M\}$ and occurs in two variants according to whether the XMX planes on the two molecules are approximately parallel (P8PE) or orthogonal (O8PE). Molecules $[M(PPh_3)_3]^z$ can form a 12PE, which uses $\{M(XPh_2)_3\}\cdots\{(Ph_2X)_3M\}$ and includes ten intermolecular **ef** interactions. The crystal packing in various compounds containing $[M(PPh_3)_3]^z$ or $[M(PPh_3)_4]^z$ is described, and involves either multiple instances of one embrace type in high symmetry crystal lattices or combinations of various multiple phenyl embraces in lower symmetry crystal lattices. The current hierarchy of multiple phenyl embraces is summarised.

In previous papers we have identified patterns of crystal packing, for a variety of compounds, which are constructed from multiple phenyl embraces.[1–5] A multiple phenyl embrace (MPE) is a supramolecular motif comprised of a set of concerted phenyl–phenyl attractions. It is well established that the most favourable attractive interactions between pairs of phenyl rings are those involving the edge-to-face (**ef**) and offset-face-to-face (**off**) geometries. In the edge-to-face geometry (and the closely related vertex-to-face geometry) the two rings are inclined to each other and H atoms of one are directed towards C atoms of the other, while in the offset-face-to-face geometry the two rings are approximately parallel and again positioned such that H atoms of one are closest to C atoms of the other. While the main component of the attractive energy is dispersion, the coulombic $H^{\delta+}C^{\delta-}$ energy provides the directionality.

A multiple phenyl embrace is a higher level of intermolecular organisation of peripheral phenyl rings. It requires that a set of phenyl rings on a molecule be correctly positioned and oriented to participate in a concerted set of intermolecular phenyl–phenyl attractive interactions with an adjacent molecule. The essential concept is that a molecular set $(Ph)_n$ be predisposed to form efficient and concerted intermolecular supramolecular attractive motifs.

The most widely occurring multiple phenyl embrace is the sextuple phenyl embrace, in which the three phenyl rings of an XPh_3 moiety are directed towards three phenyl rings from the partner XPh_3 moiety with the formation of six good intermolecular **ef** interactions.[3,4] This sextuple phenyl embrace is ubiquitous in crystals containing Ph_4P^+ cations and in molecules with the frequently used PPh_3 terminal ligand: the phenyl groups of one Ph_4P^+ can engage in several multiple phenyl embraces.[2]

We are investigating the crystal supramolecularity of molecules with more than four phenyl groups on the surface and with the potential for more elaborate multiple phenyl embraces. In this paper we focus on the subset of metal complexes with multiple PPh_3 ligands, particularly the homoleptic complexes $[M(PPh_3)_3]^z$ and $[M(PPh_3)_4]^z$, $z = 0, +1$. In these molecules the external arrays of phenyl groups and the possibilities for more elaborate multiple phenyl embraces are affected by both the conformational restrictions within PPh_3 and the stereochemistry of the metal that binds the PPh_3.

The higher order motifs that we find in these compounds prompt some reconsideration of the abbreviations for multiple phenyl embraces: we replace the adjectives quadruple and sextuple with arabic numerals, describing the multiple phenyl embraces as *n*-phenyl embraces. Thus the orthogonal quadruple phenyl embrace (OQPE[4]) becomes the O4PE, the parallel quadruple phenyl embrace (PQPE[4]) becomes the P4PE, the sextuple phenyl embrace (SPE[3,4]) becomes the 6PE, the zig-zag infinite sextuple phenyl embrace (ZZISPE[2]) becomes ZZI6PE, and the hexagonal array of sextuple phenyl embraces (HASPE[5]) becomes the HA6PE.

The larger multiple phenyl embraces described in this paper are the enlarged 6PE (abbreviated E6PE), the hybrid 6PE (H6PE), the eight-phenyl embrace with the subtypes parallel (P8PE) and orthogonal (O8PE), and the twelve-phenyl embrace (12PE).

Results

We have examined the crystal structures of homoleptic complexes of the type $[M(PPh_3)_x]^z$, where $x = 3$ or 4, with a view to recognising those extended intermolecular phenyl embraces that take place. Table 1 presents chemical compositions and crystal structure information for the relevant compounds contained (with atom coordinates) in the Cambridge Structural Database[6,7] (April, 1997). There are 15 compounds $M(PPh_3)_3$ where the metal is coordinated to three PPh_3 groups only and the geometry of the metal is more or less trigonal planar: these are $[M(PPh_3)_3]^0$, M = Ni, Pd and Pt, and $[M(PPh_3)_3]^+$, M = Rh, Cu, Ag and Au. Only two of these crystals are isostructural, leaving 14 different structures. There are ten compounds with tetrahedral $[M(PPh_3)_4]^{0,+}$, which adopt five different crystal structures. We first describe the five

† *Non-SI unit employed*: cal = 4.184 J.

Table 1 Crystal structures from the Cambridge Structural Database for compounds of the type $[M(PPh_3)_x]^z$ and three other relevant compounds

Refcode	Compound	Space group	Unit cell dimensions (a, b, c/Å, α, β, γ/°, or relevant subset)
$[M(PPh_3)_3]^z$			
AUBPHA	$[Au(PPh_3)_3]^+BPh_4^-PPh_3 \cdot CHCl_3$	$P2_1/n$	16.0, 30.0, 16.9, 90.8
BIVRUT	$[M(PPh_3)_3]^+NO_3^-$ [M = 2/3 Au, 1/3 Ag]	$P\bar{1}$	13.4, 13.9, 14.4, 64.2, 88.5, 75.5
CIDHUS	$[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^- \cdot CH_2Cl_2$	$P2_1/c$	14.8, 25.4, 17.6, 98.7
DEZYUC	$[Cu(PPh_3)_3]^+[V(CO)_6]^-$	$P\bar{1}$	11.7, 12.7, 19.4, 102.2, 92.0, 108.3
DUSZUM	$[Ag(PPh_3)_3]^+NO_3^-$	$P2_1/n$	19.0, 13.7, 17.9, 94.9
JEKCIL	$[Ni(PPh_3)_3]$	$P\bar{1}$	18.5, 16.2, 17.8, 105.9, 117.3, 92.3
LAXKIE	$[Cu(PPh_3)_3]^+[FeCl_4]^-$	$P2_1/n$	19.1, 23.4, 11.5, 98.7
SOTSID	$[Cu(PPh_3)_3]^+[(CO)_5Cr(\mu_2\text{-}H)Cr(CO)_5]^-$	$P2_1/n$	11.9, 31.5, 16.1, 90.7
TPAUPB	$[Au(PPh_3)_3]^+BPh_4^-$	$P2_1/c$	16.7, 20.6, 18.4, 95.1
TPAWTB10	$[Au(PPh_3)_3]^+[B_9SH_{12}]^-$	$P\bar{1}$	13.1, 19.6, 11.2, 103.6, 72.1, 94.8
TPPHPT01	$[Pt(PPh_3)_3]$	$P2_1/c$	21.2, 12.4, 18.6, 112.9
VACKEP	$[Pd(PPh_3)_3]$	$P\bar{1}$	11.7, 14.8, 15.8, 109.3, 95.2, 90.5
ZEPYAU	$[Au(PPh_3)_3]^+[(cp)Mo(SC_6F_5)_4]^- \cdot (CH_2Cl_2)_{0.5}$	$P\bar{1}$	11.6, 16.8, 20.0, 94.1, 93.8, 92.2
ZEPYEY	$[Cu(PPh_3)_3]^+[(cp)Mo(SC_6F_5)_4]^- \cdot (CH_2Cl_2)_{0.5}$	$P\bar{1}$	11.6, 16.9, 19.9, 94.2, 93.8, 92.3
ZETBIJ	$[Au(PPh_3)_3]^+[SiF_5]^- \cdot (CH_2Cl_2)_{1.5}$	$P\bar{1}$	14.6, 17.2, 22.2, 86.5, 79.0, 84.0
$[M(PPh_3)_4]^z$			
AUBPHB	$[Au(PPh_3)_4]^+BPh_4^- \cdot EtOH$	$Ibca$	22.2, 23.1, 30.7
AUBPHC	$[Au(PPh_3)_4]^+BPh_4^- \cdot CH_3CN$	$Ibca$	21.7, 22.9, 30.7
CUGYIM	$([Ag(PPh_3)_4]^+)_2[SnClPh_2(NO_3)_2]^-[SnPh_2(NO_3)_3]^-$	$P\bar{1}$	22.4, 14.1, 14.0, 90.6, 69.8, 64.6
DAYGIT[a]	$[Cu(PPh_3)_4]^+ClO_4^-$	$R\bar{3}$	19.0, 44.1 (rhombohedral setting)
KIDFUY	$[Cu(PPh_3)_4]^+PF_6^-$	$R\bar{3}$	19.0, 44.2
KANXUS01	$[Ag(PPh_3)_4]^+PF_6^-$	$R\bar{3}$	19.1, 44.0
DUTBAV	$[Ag(PPh_3)_4]^+NO_3^-$	$R\bar{3}$	19.1, 43.8
DAYGOZ[a]	$[Ag(PPh_3)_4]^+ClO_4^-$	$R\bar{3}$	19.1, 43.9
KUYTUT	$[Rh(PPh_3)_4]^+BH_4^-$	$P\bar{4}3n$	15.1
TTPPDB	$[Pd(PPh_3)_4] \cdot (C_6H_6)_{0.5}$	$Pa3$	22.9
Other compounds used for comparisons			
ACRHCP	$(Ph_3P)Rh(acac)(CO)$	$P\bar{1}$	13.2, 10.5, 8.9, 97.1, 110.9, 103.2
FOBLEN	$(Ph_3P)(H)Rh(PPh_2CH_2)_2Zr(cp)_2$	$P2_1/n$	12.2, 21.1, 17.6, 98.7
KIDYAX	$(Ph_3P)(Cl)Rh(Ph_2P\text{—}O\text{—}PPh_2) \cdot THF$	$P\bar{1}$	11.3, 11.5, 17.1, 102.3, 102.7, 74.1

[a] There are other isomorphous compounds $[M(XPh_3)_4]^+ClO_4^-$, which occur with M = Cu, Ag; X = As, Sb, Bi,[14] and $[M(AsPh_3)_4]^+BF_4^-$ with M = Ag, Au.[15]

new multiple phenyl embraces identified by examination of the packing in these crystals, commencing with two variants of the 6PE.

The enlarged six-phenyl embrace (E6PE)

In crystalline $[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^- \cdot CH_2Cl_2$ [CIDHUS],‡ two approximately planar $[Rh(PPh_3)_3]^+$ molecular units face each other such that each Ph_3P ligand of each molecule directs one phenyl group towards the other molecule. This results in six phenyl rings in the centrosymmetric interaction zone, with each phenyl ring inclined to the pseudo-threefold axis of the molecule so that a cycle of six intermolecular **ef** interactions forms the embrace. This is named the enlarged six-phenyl embrace, or E6PE: the enlargement relative to the 6PE occurs within each molecule, not between the molecules. The characteristics of this E6PE are shown in Fig. 1(*b*) and 2(*b*) in comparison with the 6PE: the space-filling representations reveal the quality of the individual **ef** interactions, while the skeletal pictures show the similarities and differences of the phenyl ring positions in the E6PE and the 6PE. The 6PE is $(XPh_3)\cdots(Ph_3X)$, while the E6PE is $(XPh)_3\cdots(PhX)_3$.

The close embrace of edge-to-face phenyl rings in the E6PE would be expected to be energetically favourable, and this is borne out by calculations using summed atom–atom potentials. For this E6PE the intermolecular energy is an attractive −13.4 kcal mol^{-1} per $\{(Ph)_3\cdots(Ph)_3\}$ set, compared with −12.1 kcal mol^{-1} per $\{Ph_3\cdots Ph_3\}$ set for the typical 6PE shown in Fig. 1(*a*) and 2(*a*).§

Comparison of the geometries of the 6PE and E6PE, in Fig. 3, shows that even though the P—C_{ipso} vectors for the rings involved form a large angle (*ca.* 66°) with the threefold axis in the 6PE and a substantially smaller angle (*ca.* 30°) in the E6PE, the individual **ef** interactions are not dissimilar. The Ph$\cdots$Ph intercentroid distances for the **ef** interactions in both embraces (see Table 2) are in the range 5.0–5.2 Å, but the P$\cdots$P distances in the E6PE at 8.6 ± 0.1 Å are *ca.* 2 Å longer

Table 2 Intercentroid distances (Å) for the six participating rings in the 6PE [ACRHCP] and E6PE [CIDHUS]

	6PE			E6PE		
Ring No	1	2	3	1	2	3
1	5.2	5.0	7.1	5.0	5.1	7.3
2	5.2	7.3	5.0	5.0	8.7	5.1
3	7.4	5.2	5.2	9.4	5.0	5.0

‡ The six-letter codes are the refcodes of the Cambridge Structural Database.

§ These energies are calculated with revised and improved atomic parameters, and differ from our previously reported calculated energies.

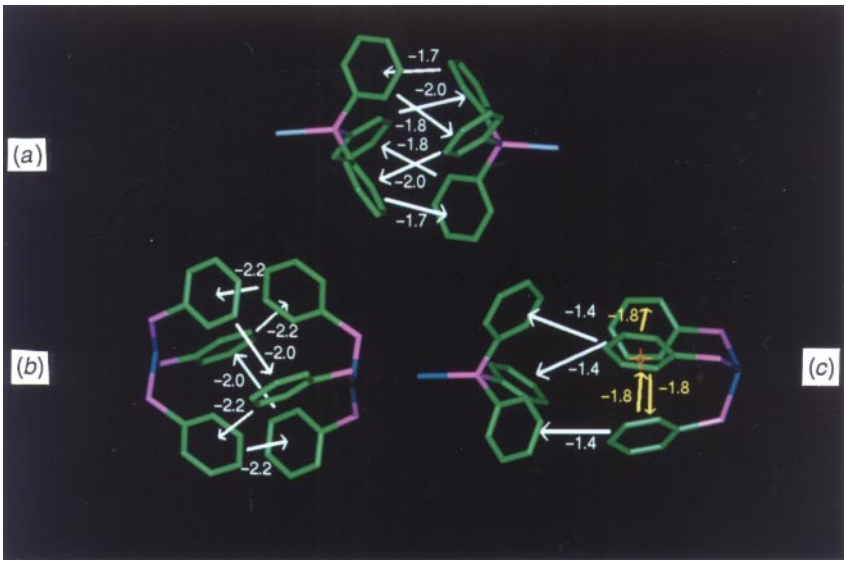


Fig. 1 A comparison of the three types of 6PE. (*a*) The traditional 6PE as illustrated in crystalline $(Ph_3P)Rh(acac)(CO)$ [ACRHCP], (*b*) the E6PE found in CIDHUS and (*c*) the H6PE found in KUYTUT, showing the major components of the interaction energies in these embraces. Edge-to-face interactions are marked with single-ended arrows, intermolecular interactions are white and intramolecular are yellow

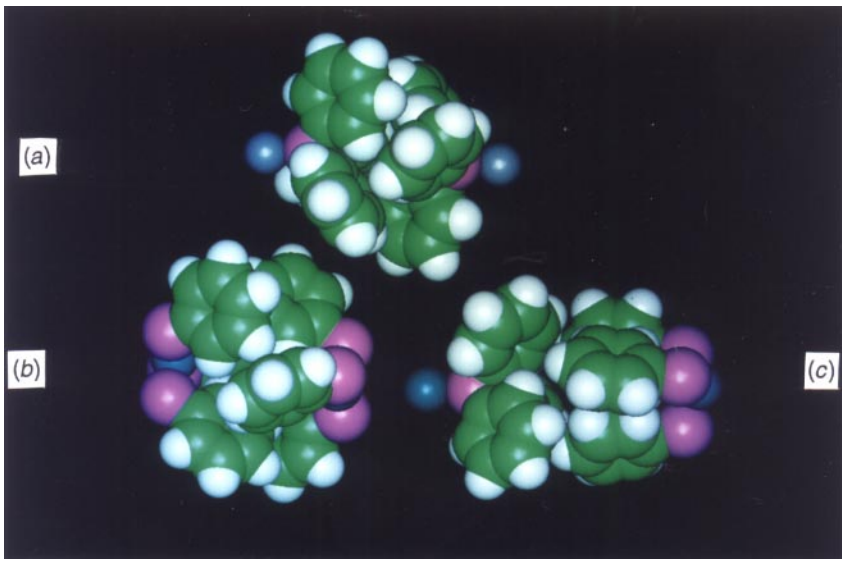
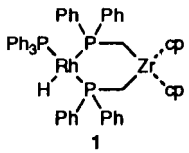


Fig. 2 A space-filling view of the three types of 6PE, oriented as in Fig. 1. (*a*) The 6PE in ACRHCP, (*b*) the E6PE found in CIDHUS and (*c*) the H6PE found in KUYTUT. The edge-to-face intermolecular interactions are clear in each of the three embraces, as are the intramolecular edge-to-face interactions in (*c*)

than the typical P···P distance in the 6PE. Since only one phenyl ring on each PPh_3 is required for the E6PE, it is conceivable that the E6PE could occur for molecules with less phenylated phosphine ligands, and it does. The compounds **1** [FOBLEN] and **2** [KIDYAX], in which two of the PPh_3 ligands have been replaced with Ph_2P—bridge—PPh_2, both demonstrate E6PEs.



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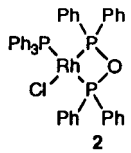

2

The hybrid six-phenyl embrace (H6PE)

In crystalline $[Rh(PPh_3)_4]^+BH_4^-$ [KUYTUT], there is a different type of 6PE, shown in Fig. 1(*c*) and 2(*c*), in which three Ph from one PPh_3 on one side of the interaction domain are directed towards three Ph from three different PPh_3 ligands on a second molecule on the other side. The intermolecular phenyl–phenyl interactions are edge-to-face and there are three of them; in addition there is a cycle of three intramolecular **ef** interactions between the rings of the three different PPh_3 ligands [see Fig. 1(*c*)]. This 6PE is a hybrid of the standard 6PE with one XPh_3 on either side, and the E6PE with three XPh on either side, and therefore is dubbed the hybrid six-phenyl embrace, H6PE. In the notation where the 6PE is $(XPh_3)\cdots(Ph_3X)$ and the E6PE is $(XPh)_3\cdots(PhX)_3$, the H6PE is $(XPh)_3\cdots(Ph_3X)$. Note from Fig. 1 and 2 that the P—C_{ipso} vectors on the $(PPh)_3$ side of the H6PE are approximately parallel to the pseudo-threefold axis, not splayed at the angles of 30° as occurs in the E6PE.

The calculated energy for this H6PE is made up of two components: the intermolecular one of -7.8 kcal mol^{-1} per $Ph_3\cdots(Ph)_3$ unit and the additional intramolecular one of -5.4 kcal mol^{-1} for the $(Ph)_3$ portion of the embrace. The total energy of the embrace is therefore -13.2 kcal mol^{-1} per $\{Ph_3\cdots(Ph)_3\}$ set.

The eight-phenyl embraces (P8PE and O8PE)

An eight-phenyl embrace (8PE) involves two PPh_2 units connected by a metal atom in each molecule, and therefore eight

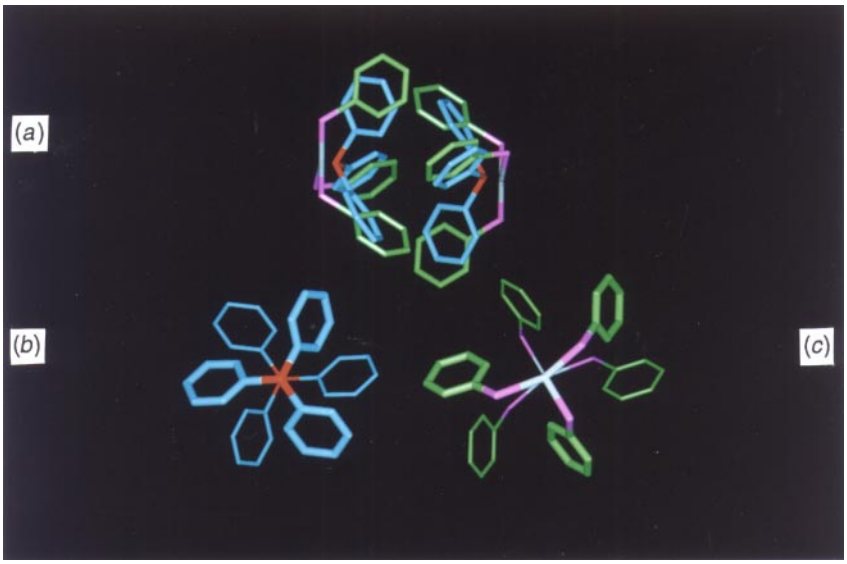

Fig. 3 Geometrical comparison of the E6PE in $[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^- \cdot CH_2Cl_2$ [CIDHUS] (phenyl rings green) and the 6PE (phenyl rings blue) in $PPh_3Rh(acac)(CO)$ [ACRHCP], to show the different orientations of the phenyl rings but the similar **ef** interactions. (*a*) Side view of the E6PE and the 6PE superimposed; (*b*) projection along the axis of the 6PE; (*c*) projection along the axis of the E6PE. Note that the planar coordination around Rh in $[Rh(PPh_3)_3]^+$ is substantially distorted from trigonal at Rh (coloured silver), but this does not interfere with the E6PE

phenyl rings as $\{M(PPh_2)_2\}\cdots\{(Ph_2P)_2M\}$ in the embrace domain. We observe two types of 8PE, depending on the relationship between the two PMP planes, one in each molecule, and these two types are portrayed in Fig. 4 and 5. In the parallel 8PE (P8PE) the two PMP planes are exactly or approximately parallel, and the four P atoms of the embrace are approximately coplanar [Fig. 4(*a*)]. This allows eight intermolecular **ef** interactions in the embrace, but the set of **ef** interactions is not cyclic as it is in a 6PE. For the P8PE in crystalline $[Pd(PPh_3)_3]$ [VACKEP], $M\cdots M = 11.9$ and $P\cdots P = 9.2$ Å, and the calculated intermolecular energy for the $(Ph_4)_2$ pair is -14.1 kcal mol^{-1}. There are also **ef** and **off** interactions between the PPh_2 groups within one $Pd(PPh_3)_3$ molecule, as shown on Fig. 4(*a*), and the total energy between the eight phenyl rings in the interaction zone is -22.5 kcal mol^{-1}. The two $M(PPh_2)_2$ foundations of the 8PE need not be coplanar as in the P8PE, but can be approximately orthogonal, such that the four P atoms constitute a tetrahedron elongated along the embrace axis. The resulting orthogonal 8PE (O8PE) is shown in Fig. 4(*b*) and 5(*b*), as it occurs in crystalline $[Au(PPh_3)_4]^+BPh_4^- \cdot EtOH$ [AUBPHB]. The P8PE ⇔ O8PE relationship is analogous to the P4PE ⇔ O4PE relationship for four-phenyl embraces.[4] In the O8PE of AUBPHB two of the intermolecular interactions are face-to-face. The calculated intermolecular energy for a $(Ph_4)_2$ pair is -11.5 kcal mol^{-1}. As in the P8PE, there are also intramolecular interactions between the PPh_2 groups in the interaction domain, the major interactions being edge-to-face [Fig. 4(*b*)], which contribute -4.3 kcal mol^{-1} for each molecule, and so the total energy between the eight phenyl rings in the interaction zone is -20.1 kcal mol^{-1}.

The twelve-phenyl embrace (12PE)

In molecules $[M(PPh_3)_3]^z$ with planar stereochemistry one of the intermolecular variables is torsion around M—P bonds. This intramolecular variable affects the intermolecular multiple phenyl embraces, and is assessed in terms of the directions of the P—C_{ipso} bonds and thus the positions of the phenyl rings relative to the MP_3 plane. In $[Rh(PPh_3)_3]^+$, as it occurs in CIDHUS, there are three rings approximately in the MP_3 plane and three rings on either side. However, in $[Pd(PPh_3)_3]$ [VACKEP] six phenyl rings are splayed to one side of the MP_3 plane, and these six phenyl rings form three **off** pairs *within* each molecule. In VACKEP these $(PPh_2)_3$ faces come together to form a centrosymmetric twelve-phenyl embrace (12PE). Fig. 6(*a*) is a side view of this embrace with arrows marking the ten **ef** interactions, while Fig. 6(*b*) is a space-filling view from the same direction. Fig. 7 shows the skeleton of the embrace viewed normal to the two molecular planes, with the individual phenyl–phenyl interactions identified with their calculated attractive energies. The combination of intramolecular **off** and intermolecular **ef** interactions in the 12PE creates a ring of double herringbone Ph–Ph interactions [evident in Fig. 6(*b*)] analogous to the double herringbone known in crystalline aromatic hydrocarbons.[8–11]

The 12PE differs from the 6PEs in that the pseudo-threefold axes of the two molecules are not colinear, and as a consequence there is not a continuous cycle of intermolecular phenyl–phenyl interactions: there are ten **ef** interactions between the twelve phenyl rings in this 12PE. The total energy of the $(Ph_6)_2$ pair in VACKEP is calculated to be -17.7 kcal mol^{-1}. When the intramolecular energies between phenyl rings within the interaction area are included the total phenyl–phenyl interaction energy for a pair of molecules is -37.5 kcal mol^{-1} (the contribution of the three **ef** interactions on the distal side of each molecule is not included in this total).

Having described these additional multiple phenyl embraces revealed in compounds containing $[M(PPh_3)_3]^z$ or $[M(PPh_3)_4]^z$ some broader questions arise. From Table 1 it is evident that the $[M(PPh_3)_3]$ compounds with no anion or with a simple threefold anion do not have high crystal packing symmetry, whereas the $[M(PPh_3)_4]$ compounds do have high crystal lattice symmetry. This raises questions about intramolecular stereochemistry as it could affect embrace formation and thereby the crystal packing. In this, as in all crystal supramolecularity,[1] there is the underlying question about whether molecular stereochemistry determines crystal packing, or *vice versa*. In this context we note that the three $[M(PPh_3)_3]^0$ compounds, M = Ni, Pd and Pt, have different crystal lattices and low symmetry, while crystals of $[M(PPh_3)_4]^+$, M = Cu, Ag and Au, with various anions have high symmetry and are isostructural.

Accordingly, we first analyse intramolecular geometries in relation to the occurrence of the various intermolecular multiple phenyl embraces, and then describe the crystal packing in

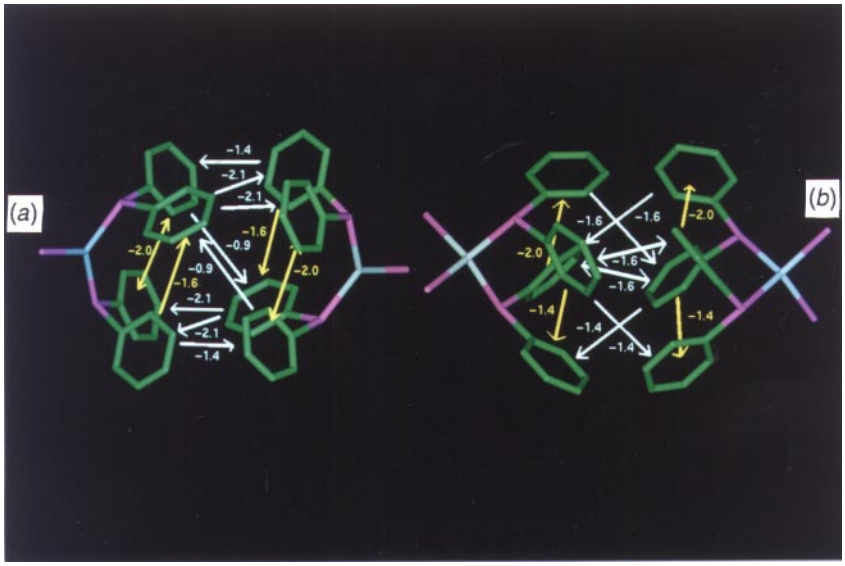

Fig. 4 A comparison of the two different 8PE. (*a*) The centrosymmetric P8PE in $[Pd(PPh_3)_3]$ [VACKEP] and (*b*) the O8PE found in $[Au(PPh_3)_4]^+BPh_4^- \cdot EtOH$ [AUBPHB]. Edge-to-face interactions are marked with single-ended arrows, face-to-face with double-ended arrows, intermolecular interactions are white and intramolecular are yellow

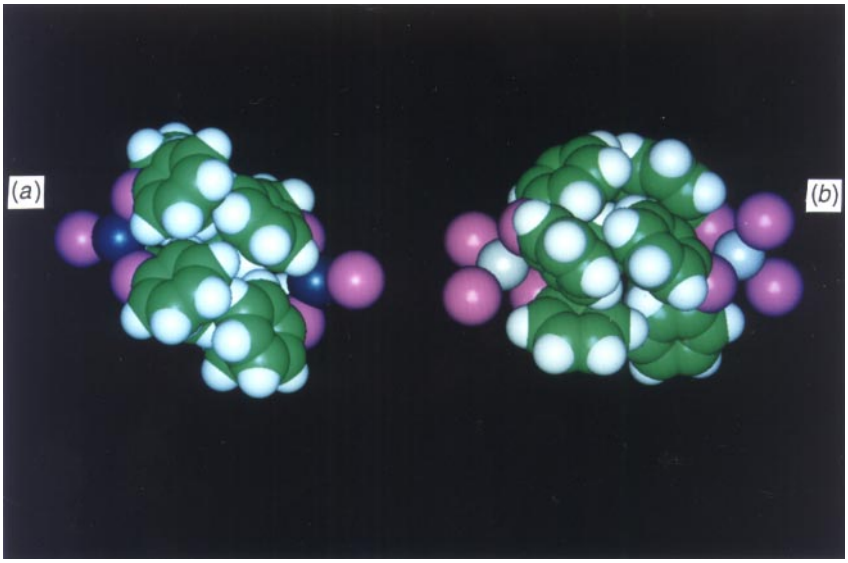

Fig. 5 A space-filling view of the two types of 8PE. (*a*) The P8PE in VACKEP and (*b*) the O8PE found in AUBPHB. The edge-to-face intermolecular interactions in VACKEP are clear, as are the face-to-face interactions in AUBPHB

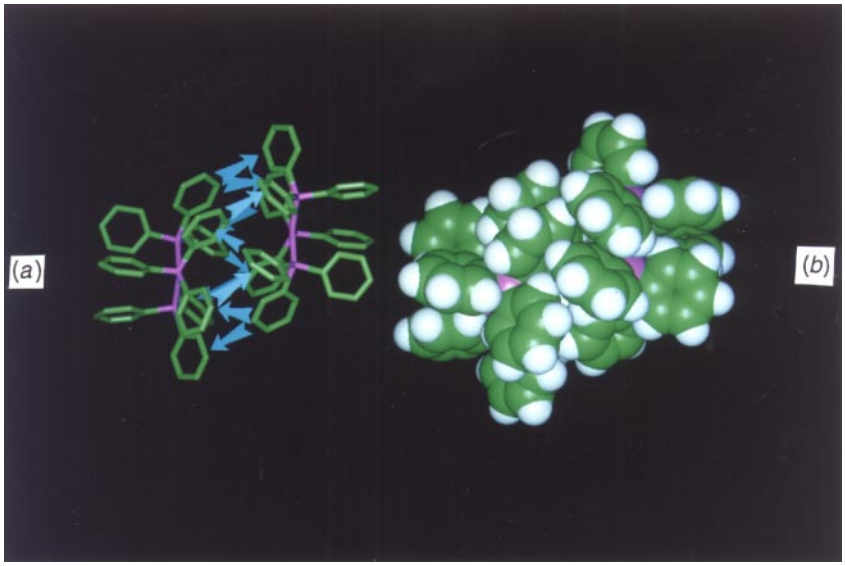

Fig. 6 (*a*) Side view of the twelve-phenyl embrace of two molecules of $[Pd(PPh_3)_3]$ [VACKEP]: hydrogen atoms not shown. (*b*) Space-filling representation of the 12PE in the same orientation as (*a*), with hydrogen atoms included

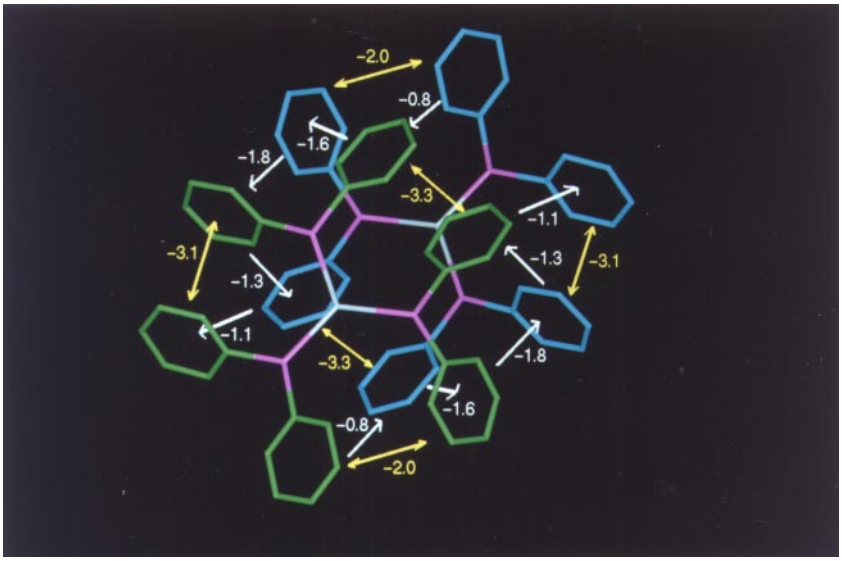

Fig. 7 The 12PE in crystalline $[Pd(PPh_3)_3]$ [VACKEP] viewed normal to the coordination planes: phenyl rings in the upper molecule are coloured green, those in the lower molecule blue. Attractive energies [kcal (mol Ph_2)$^{-1}$] within each molecule are marked on double-ended yellow arrows (**off** interaction), and between the molecules on white arrows for the ten **ef** interactions. Note the displacement of the molecular threefold axes

key compounds. The occurrences of the multiple phenyl embraces in the relevant crystals are shown in Table 3.

Intramolecular geometry of $[M(PPh_3)_x]^z$ systems in relation to multiple phenyl embraces

A $[M(PPh_3)_3]$ molecule has several degrees of conformational freedom while retaining approximately planar MP_3 coordination. Fig. 8 shows the molecular structures of $[M(PPh_3)_3]^0$ for M = Ni, Pd and Pt, and it is evident that there is structural variability in the array of nine phenyl groups. This arises because these nine phenyl rings are not tightly packed, and various loose intramolecular **ef** and **off** interactions can be adopted. $[Pt(PPh_3)_3]$ has three Ph rings directed to each side of the MP_3 plane and three around the girdle of the molecule. In $[Ni(PPh_3)_3]$ two rings on adjacent P atoms take part in **off** interactions. It is also possible to have three sets of **off** phenyl rings on the molecule, as found in $[Pd(PPh_3)_3]$, and in this case there are six rings on one side of the MP_3 plane and three on the other, and therefore this molecule can, and does, take part in a 12PE. Two other structures exhibit the molecular structure of $[Pd(PPh_3)_3]^0$, namely BIVRUT and AUBPHA (see Table 1 for chemical composition), and in the case of BIVRUT a less effective 12PE occurs. AUBPHA has an uncoordinated PPh_3 ligand that is positioned over the Au atom (but with P···Au = 3.95 Å) on the side of the molecule that might take part in a 12PE. A result of having six rings oriented to one side of the MP_3 plane is that the remaining three rings project from the other side to form a cycle of three **ef** interaction [see Fig. 8(*a*) for Pd] and can form an H6PE. This does occur in AUBPHA, with the other three phenyl rings coming from the anion BPh_4^-. The molecular structures of all examples of $[M(PPh_3)_4]$ are very similar, for the reason that the phenyl rings on the surface of the molecule are quite closely packed as a concerted intramolecular array of well-developed local **ef** interactions. Some of these are illustrated in Fig. 9(*a*). Each of the tetrahedral faces exhibits an arrangement of Ph rings in which three P—C vectors are perpendicular to the P_3 plane [Fig. 9(*b*)] appropriate for formation of an H6PE. In several cases, H6PEs are, in fact, formed: cation···cation in the case of KUYTUT and cation···anion (with BPh_4^-) in the case of AUBPHB, AUBPHC and TPAUPB.

Table 3 Occurrence of phenyl embraces in some compound of the type $[M(PPh_3)_3]^z$ and $[M(PPh_3)_4]^z$

Crystal	Compound	4PE	6PE	E6PE	H6PE	P8PE	12PE
$M(PPh_3)_3$							
JEKCIL	$[Ni(PPh_3)_3]$		X				
VACKEP	$[Pd(PPh_3)_3]$	X				X	X
TPPHPT01	$[Pt(PPh_3)_3]$	X					
AUBPHA	$[Au(PPh_3)_3]^+BPh_4^-PPh_3\cdot CHCl_3$	X	X (to BPh_4)		X (to BPh_4)		
BIVRUT	$[M(PPh_3)_3]^+NO_3^-$ [M = 2/3 Au, 1/3 Ag]		X			X	X (inferior)
DEZYUC	$[Cu(PPh_3)_3]^+[V(CO)_6]^-$	X				X	
LAXKIE	$[Cu(PPh_3)_3]^+[FeCl_4]^-$	X	X				
TPAUPB	$[Au(PPh_3)_3]^+BPh_4^-$		X		X (distorted) (to BPh_4)		
CIDHUS	$[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^-\cdot CH_2Cl_2$		X	X			
$M(PPh_3)_4$							
DAYGIT	$[Cu(PPh_3)_4]^+ClO_4^-$					X	
KUYTUT	$[Rh(PPh_3)_4]^+BH_4^-$				X		
AUBPHB	$[Au(PPh_3)_4]^+BPh_4^-\cdot EtOH$		X (to BPh_4)		X (to BPh_4)	X (O8PE)	
CUGYIM	$([AgPPh_3)_4]^+)_2[SnClPh_2(NO_3)_2]^-[SnPh_2(NO_3)_3]^-$		X			X	
TTPPDB	$[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$					X	

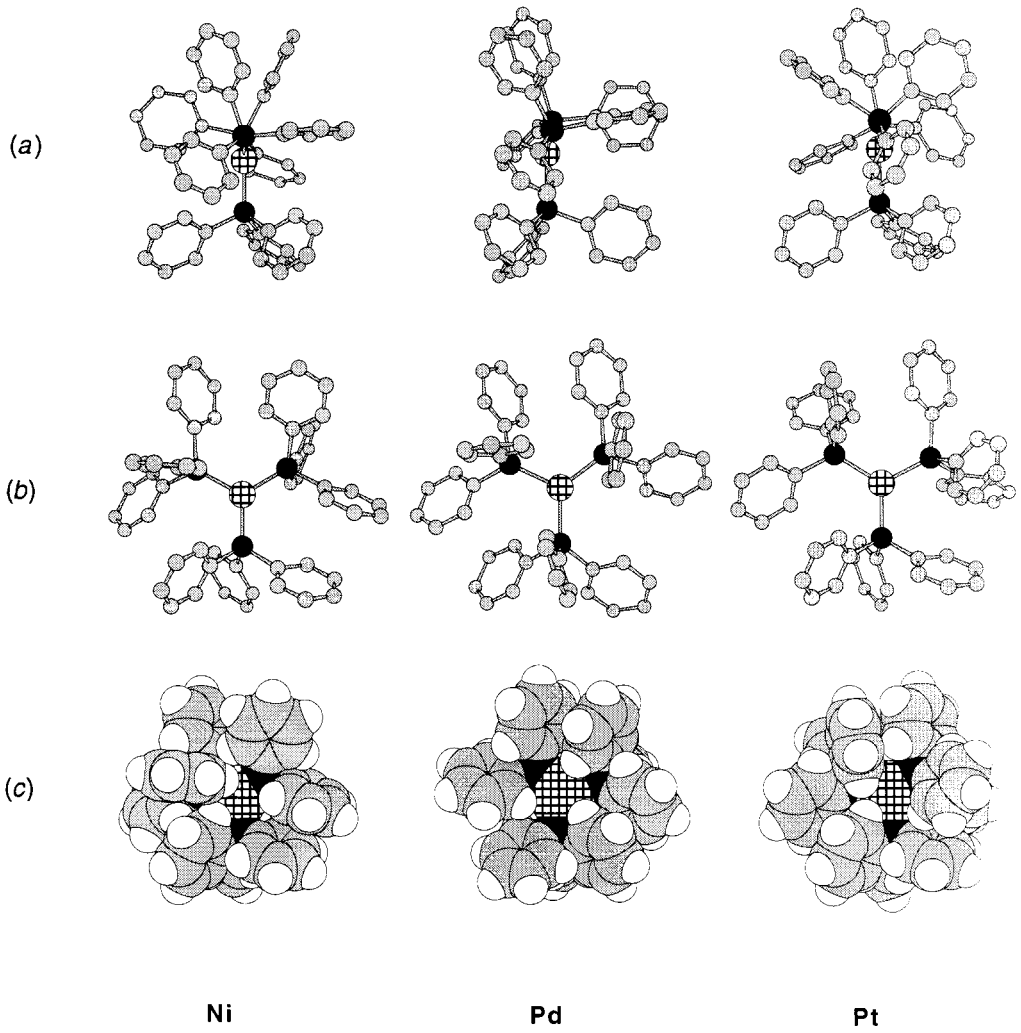

Fig. 8 Molecular structures of $[M(PPh_3)_3]^0$, M = Ni, Pd and Pt, viewed parallel and perpendicular to the MP_3 plane to show the locations and orientations of the nine phenyl rings relative to this plane and the intramolecular Ph–Ph interactions in **off** and **ef** geometries. The pictures in row (*a*) are rotated 90° about the axis that is vertical in row (*b*). The space-filling representations with hydrogen atoms in row (*c*) give the same orientation as row (*b*) except for Pd where the view in (*c*) is from the reverse side to show the prominent three pairs of **off** interactions directed to one side of the PdP_3 plane. In $[Pd(PPh_3)_3]$ the remaining three rings have their P—C vectors approximately perpendicular to the MP_3 plane and form a cycle of **ef** interactions

The arrangement of phenyl rings required for an P8PE is more easily accommodated. Two P atoms of one molecule need to be approximately coplanar with two from a second molecule, such that two of the P···P distances are of the order of 9 Å and the M···M distance is about 12 Å. Since the pairs of P atoms are linked by a metal, it is easy for two of the rings on each P atom to be directed towards the interaction zone, thus forming an 8PE with a variety of ring–ring interactions

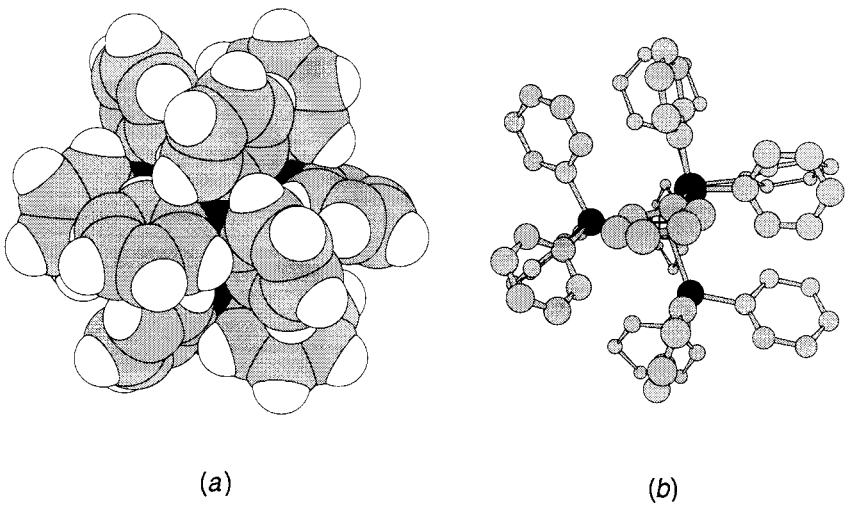

Fig. 9 Molecular structure of $[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$ [TTPPDB] viewed from two different directions. (*a*) Space-filling threefold representation that makes the concert of local **ef** interactions between Ph rings clearly evident. (*b*) Side view with H atoms omitted: note the similarity between the right side of this portrayal and the corresponding side view of $[Pd(PPh_3)_3]$ in Fig. 8(*a*)

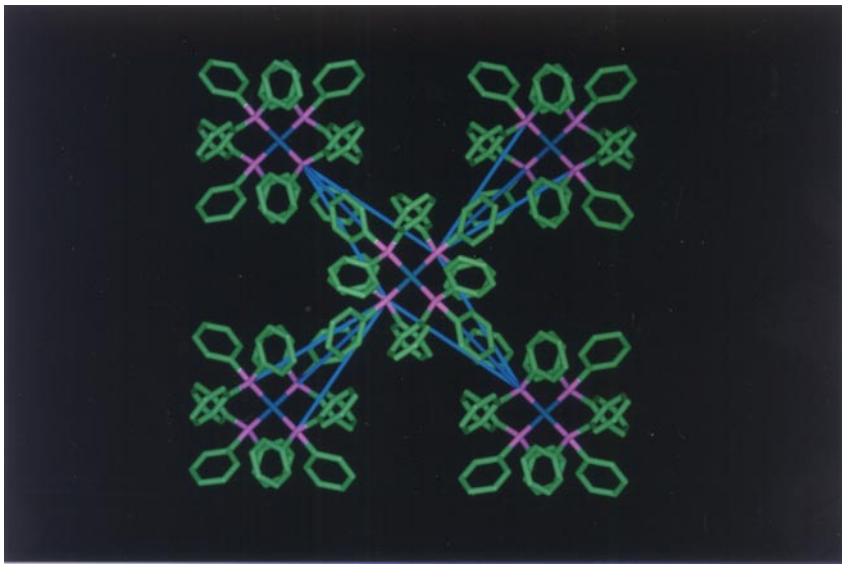

Fig. 10 A central molecule of $[Rh(PPh_3)_4]^+$ in KUYTUT with four of the surrounding molecules. Two of these take part in H6PE with the central molecule providing the $-PPh_3$, and two have the central molecule supplying the three PPh groups. Each H6PE is designated by three blue lines joining the single $-PPh_3$ with the three PPh groups. Omitted from the figure are four more molecules taking part in a further four embraces to the central molecule, but located below the level shown

being possible. The ease of facilitation of the 8PE is born out by its relatively frequent occurrence. If the two sets of P—M—P are approximately orthogonal instead of parallel, an O8PE results. The E6PE, on the other hand, requires that there be only three rings on one side of the $[M(PPh_3)_3]$ molecule and that, in addition, they present the correct relative orientation to form the embrace. This type of interaction is relatively rare.

Crystal packing of multiple phenyl embraces

In the following we first describe the crystal packing in some high symmetry lattices for $[M(PPh_3)_3]$ and $[M(PPh_3)_4]$, where there is generally only one type of MPE, occurring many times. $[Rh(PPh_3)_4]^+BH_4^-$ [KUYTUT] crystallises with cubic symmetry, space-group $P\bar{4}3n$, with *each* molecule participating in *eight* H6PEs. The molecules have exact symmetry T. For four of these eight H6PEs the molecule supplies the single PPh_3, and in the other four provides the triplet of PPh groups. Each of the two types of interaction is disposed tetrahedrally around the Rh atom to constitute the cubic array, half of which is shown in Fig. 10.

The compound $[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$ [TTPPDB] also crystallises in a cubic space group, $Pa3$, in which the $[Pd(PPh_3)_4]$ molecules have symmetry C_3. Each edge of the cubic array of molecules is a P8PE, and each molecule is engaged in six P8PEs, one extending from each edge of the PdP_4 coordination tetrahedron. The benzene molecule is located at the centre of the rhombohedron and is not disordered. This benzene molecule is surrounded by phenyl rings and takes part in nine **ef** interactions: see Fig. 11. For six of these interactions, three Ph rings are above the benzene plane and three are below, with the benzene acting as the acceptor for each **ef** interaction. The other three interactions are around the periphery of the benzene, which is the donor in the **ef** interaction. The contribution to the packing energy for benzene is -14.1 kcal mol^{-1}.

Table 1 lists the isomorphous rhombohedral compounds $[M(PPh_3)_4]^+$, M = Cu, Ag and Au, crystallised with various

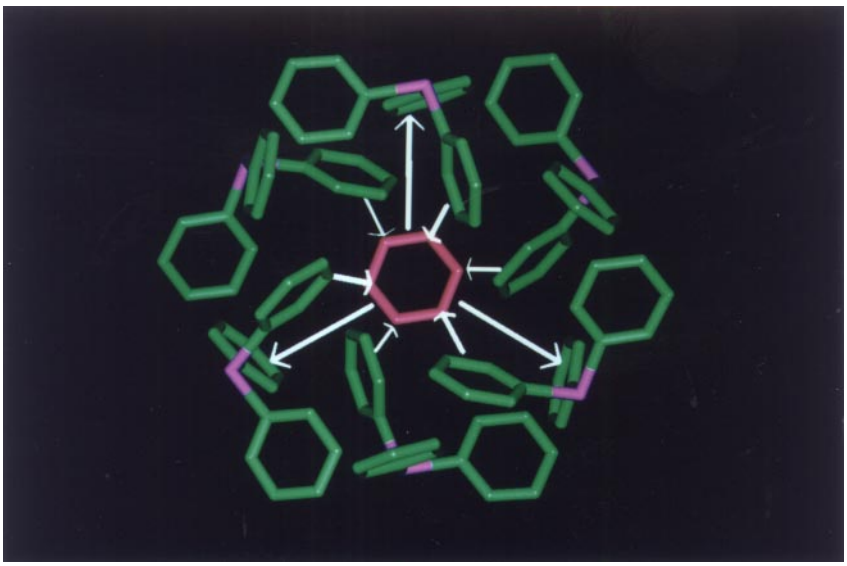

Fig. 11 The environment of the included benzene molecule in TTPPDB. The benzene is coloured pink and it is surrounded by six $-PPh_3$ groups. The nine **ef** interactions are marked with arrows

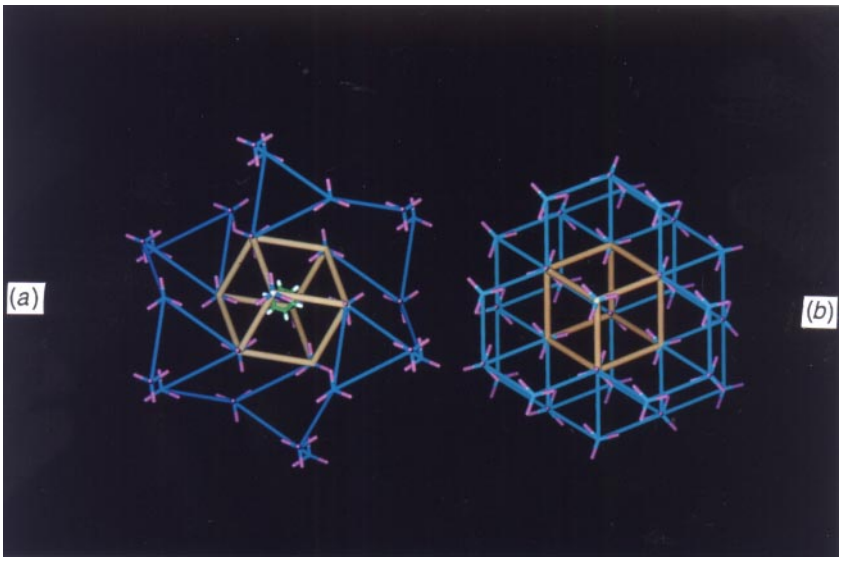

Fig. 12 The structures of (*a*) $[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$ [TTPPDB] and (*b*) $[Cu(PPh_3)_4]^+ClO_4^-$ [DAYGIT] viewed nearly down the threefold axes of their cubic and rhombohedral cells. Only the metal and P atoms are shown, with M···M linkage indicating the P8PE embraces. A cube of embraces in each structure has been highlighted with brown linkages. One included benzene molecule in TTPPDB is shown

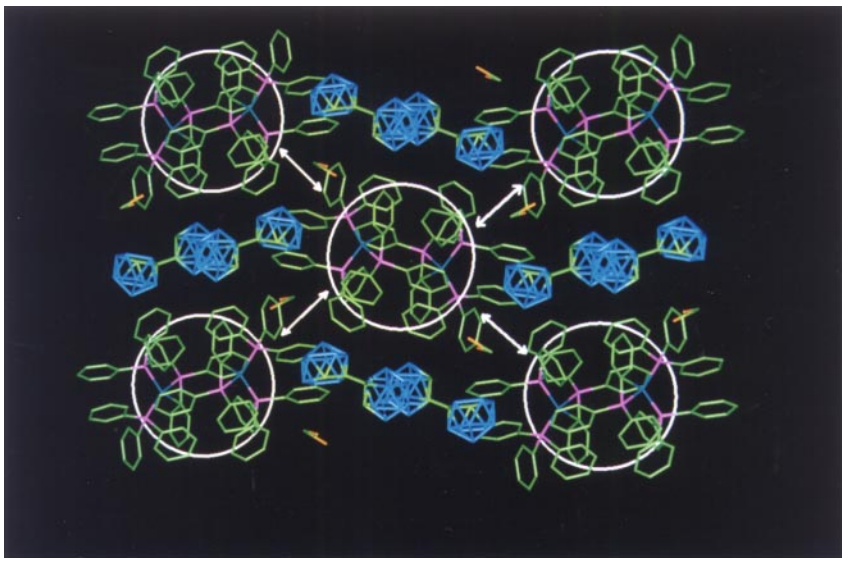

Fig. 13 Crystal packing in $[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^-\cdot CH_2Cl_2$ [CIDHUS]. Circles enclose the E6PE while arrows indicate the location of the 6PEs

small anions, which also have a high symmetry ($R\bar{3}$) lattice. The array of embraces is similar to that in $[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$. Again there are P8PEs along the edges of a rhombohedron of molecules, and the centre is occupied by the counter anion, rather than benzene. In this case, however, the rhombohedron is composed of sides of two slightly different lengths (M···M = 11.78 and 12.00 Å, for DAYGIT), making up shorter and longer P8PEs (with P···P = 8.90 and 9.21 Å, respectively). The longer 8PEs make up the six-membered ring, whose axis of symmetry aligns with the threefold axis of the cell. The rhombohedral array of P8PE in this structure type is very similar geometrically (M···M and P···P distances) to that described above for TTPPDB. In addition, the diagonal lengths of the rhombohedra are virtually identical: 25.6 Å for the long diagonal and 18.6 Å for the short diagonal in DAYGIT, compared with corresponding values of 25.7 and 18.7 Å for TTPPDB. Fig. 12 compares the cubic arrays and their environments in the two structure types. While these high symmetry structures contain multiple occurrences of the same embrace, other compounds, with lower crystal symmetry, incorporate more than one type of embrace within their lattices.

The crystal packing of $[Rh(PPh_3)_3]^+[C_4B_{19}H_{22}]^-\cdot CH_2Cl_2$ [CIDHUS] exhibits E6PEs and also contains normal 6PEs linking the pairs of molecules engaged in the E6PE, as shown in Fig. 13. As seen from Table 3, VACKEP, $[Pd(PPh_3)_3]$, has molecules linked by three different phenyl embraces, the 4PE, the 8PE and the 12PE. The way in which the 8PE and 12PE are linked is shown in Fig. 14. A pair of molecules in a 12PE also engage in a P8PE to four surrounding molecules. The crystal structure of $[Au(PPh_3)_4]^+BPh_4^-$ [AUBPHB] is an interesting combination of homogeneous (cation···cation) and heterogeneous (cation···anion) embraces, as shown in Fig. 15. Each metal centre takes part in four embraces to different BPh_4^- anions. Two of these are 6PE and two are H6PE. The four anions involved form the base of a square pyramid whose apex is occupied by the $[Au(PPh_3)_4]^+$ molecule. Distal to the four anions, the central $[Au(PPh_3)_4]^+$ molecule takes part in two O8PE to two different molecules. In all, each cation is involved in six embraces.

Summary and Discussion

We have identified five new multiple phenyl embraces contain-

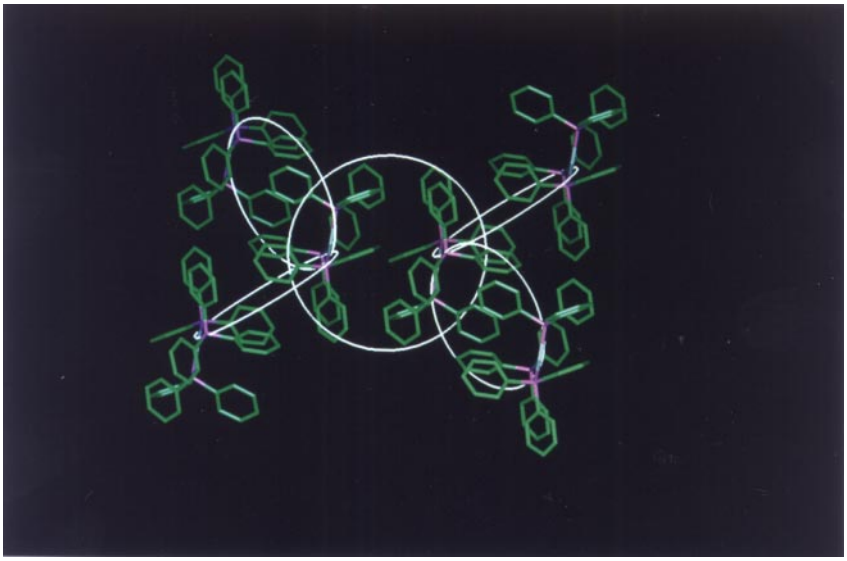

Fig. 14 The main features of the crystal packing of $[Pd(PPh_3)_3]$ [VACKEP]: the 12PE is enclosed in the circle and the P8PEs in the ellipses. There is also an O4PE, not shown

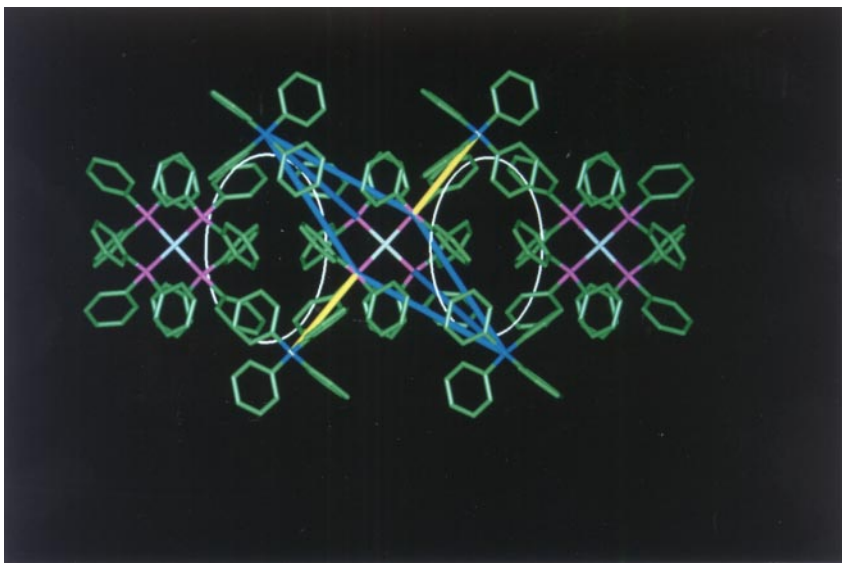

Fig. 15 The central molecule of $[Au(PPh_3)_4]^+$ in $[Au(PPh_3)_4]^+BPh_4^- \cdot EtOH$ [AUBPHB] takes part in six phenyl embraces. Two are 6PE, shown as single yellow lines, two are H6PE, shown as triplets of blue lines, and the remaining two are O8PE, shown as ellipses

ing six, eight or twelve phenyl groups. The H6PE and P8PE have a more general occurrence, but we know of only a few instances of the E6PE, O8PE and 12PE. We are looking for further examples of these embraces. We can conceive of linkages and infinite sequences involving these new embraces. For example, a molecular entity $[M(PPh_3)_3]^z$ with six Ph rings forming a 12PE on one side of the MP_3 plane has its three Ph rings on the distal side of the plane correctly positioned for a H6PE, and sequences of —H6PE—12PE—H6PE—12PE— are possible, although not observed yet.

With the recognition of the more elaborate multiple phenyl embraces described in this paper, it is appropriate to consider the heirarchy of supramolecular embrace motifs, which are based on the attractions between two phenyl groups. These are listed in Table 4, which includes the abbreviated structural formulas we use for them. Excluded from this list are the supramolecular motifs that combine phenyl groups with other molecular functionalities. The molecular components of many of the crystals considered in this study are heavily coated with phenyl groups and thus are able to participate in higher order multiple phenyl embraces. This raises questions about larger globular molecules coated with phenyl groups of phenyl-bearing ligands and their participation in multiple phenyl embraces. In this paper we have focussed on $[M(PPh_3)_3]^z$ and $[M(PPh_3)_4]^z$ but there are polymetal clusters that are heavily coated with PPh_3 ligands, and at least some of these engage in multiple phenyl embraces. However, large globular molecules require small co-crystallising partners to maintain crystal packing density and the local intermolecular contacts. Exceptions are compounds of the type $[M(PPh_3)_3]^0$, where all of the supramolecular interactions involve only phenyl rings, which shield and enclose the M and P atoms. This invites comparison with the geometry and energy of the crystal packing of benzene and other aromatic molecules.[9,10,13] The key difference is the occurrence of constrained ring orientations in $[M(PPh_3)_3]$, which is therefore exemplary of concerted multiple phenyl embraces.

In the compounds discussed in this paper, high symmetry lattices involve repetitions of one type of multiple phenyl embrace, while various embraces are combined in lower symmetry crystal lattices. We do not understand the causes of the differences between the crystal and molecular structures of $[M(PPh_3)_3]^0$ for M = Ni, Pd and Pt. We note that another polymorph of the Pt compound is mentioned without details in the Cambridge database, and we suggest that the crystallography of these compounds should be investigated further.

The compounds and crystal structures described in this paper illustrate well the essence of multiple phenyl embraces,

Table 4 The hierarchy of supramolecular embraces involving only phenyl groups

Structural formula	Multiple phenyl embrace	Comment
Between two molecules		
$(XPh_m)\cdots(Ph_mX)$	m = 1, 2, 3 in 2PE, 4PE, 6PE	Parallel (P4PE) and orthogonal (O4PE) variants of the 4PE
$(XPh)_3\cdots(PhX)_3$	E6PE	
$(XPh_3)\cdots(PhX)_3$	H6PE	
$\{(XPh_2)_2\}\cdots\{(Ph_2X)_2\}$	8PE	Parallel (P8PE) and orthogonal (O8PE) variants of the 8PE
$\{(XPh_2)_3\}\cdots\{(Ph_2X)_3\}$	12PE	
One-dimensional sequences		
$_{\infty 1}\{O4PE\}$	Linear infinite 4PE, LIT4PE, as translationally repeated O4PE	Occurs in compounds containing XPh_4 moities[2]
$_{\infty 1}\{6PE\}$	Zig-zag infinite 6PE: ZZI6PE	Common in Ph_4P^+ salts
Two-dimensional sequences		
$_{\infty 1}\{6PE\} + 4PE$ $_{\infty 2}\{4PE\}$	ZZI6PE connected by 4PE in layers	Occurs with a diverse range of anions[12] Combinations of P4PE and O4PE can be found[12]
Three-dimensional sequences		
$_{\infty 3}\{6PE\}$	Hexagonal array of 6PE: HA6PE	Common in compounds containing Ph_3XR with threefold molecular symmetry
$_{\infty 3}\{H6PE\}$	Cubic array of H6PE	In $[Rh(PPh_3)_4]^+BH_4^-$ [KUYTUT]
$_{\infty 3}\{P8PE\}$	Rhombohedral array of P8PE	In $[Cu(PPh_3)_4]^+ClO_4^-$ [DAYGIT and isomorphous structures] and $[Pd(PPh_3)_4](C_6H_6)_{0.5}$ [TTPPDB]
$(_{\infty 1}\{6PE\})_{2(orthogonal)} + 4PE$	Orthogonal ZZI6PE linked by 4PE	In $[Ph_4P]_2[CdBr_4]$[5] and a diverse range of other compounds

that is concerted phenyl–phenyl attractions using the same local interactions as occur in crystalline aromatics, but in higher order aggregates. Thus the 12PE is comprised of intramolecular **off** and intermolecular **ef** interactions forming a ring of double herringbone Ph–Ph interactions analogous to the double herringbone known in crystalline aromatic hydrocarbons. The crystal structures of $[Pd(PPh_3)_3]$ and $[Pd(PPh_3)_4]\cdot(C_6H_6)_{0.5}$ involve Ph–Ph as the only local interaction, as in crystalline benzene, but organised as 4PE, 8PE, and 12PE.

We are thinking about crystal engineering using the new embraces reported here.

Acknowledgements

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