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Metal Sandwich Molecules: Planar Metal Atom Arrays between Aromatic Hydrocarbons

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Sandwich molecules M_nS_2 consisting of a layer of transition metal atoms M (palladium) between planar polyacene aromatic hydrocarbon molecules (S) are studied using *ab initio* density functional theory. The polyacenes range from tetracene $C_{18}H_{12}$ (four rings) to circumcoronene $C_{54}H_{18}$ (nineteen rings). Geometry optimization shows that in simple arrangements, where one metal is assigned to each ring, there is a preference for metal atoms to coordinate to carbon atoms on the circumference of the sandwich. This can result in metal-metal distances greater than in bulk metal and so the establishment of planar metal clusters with metal-metal bonds in small systems is frustrated. This effect is studied by changing the number of metal atoms and relaxing symmetry constraints. A neutral molecule $Pd_5(C_{18}H_{12})_2$ with C_{2v} symmetry and a lopsided arrangement of metal atoms is shown to be consistent with experimental work on dications by Murahashi *et al.* [Science 313 (2006) 1104–1107]. In tetracene sandwiches with $n = 5$ and 9 the palladium atoms adopt η^2 - and η^3 -coordination to the edge carbon atoms. In addition to edge bonding, motifs for interior metal atoms are identified from a series of sandwiches with increasing size containing: coronene ($C_{24}H_{12}$), ovalene ($C_{32}H_{14}$), circumanthracene ($C_{40}H_{16}$) and circumcoronene ($C_{54}H_{18}$). [doi:10.2320/matertrans.48.693]

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1. Introduction

This paper reviews the status of an *ab initio* and density functional theory (DFT) study of the properties of molecules $M_n(S)_2$ in a sandwich structure, that is with an array of metal atoms M between planar aromatic hydrocarbon molecules S. Geometry is the focus of this report. We consider only sandwiches with identical outer molecules of the polyacene class. The basic geometry is shown as in Fig. 1A. There is a layer of metal atoms (central layer) sandwiched between planar aromatic molecules. The top left Fig. 1B, shows the manifold of electronic states schematically subdivided into σ - and π -levels of the carbon framework and a d-manifold of metal atom levels. The aromatics considered explicitly are from Fig. 1: tetracene $C_{18}H_{12}$ (Fig. 1C) the smallest with four rings, coronene $C_{24}H_{12}$ (Fig. 1D), ovalene $C_{32}H_{14}$ (Fig. 1E), circumanthracene $C_{40}H_{14}$ (Fig. 1F) and circumcoronene $C_{54}H_{24}$ (Fig. 1G) the largest with nineteen rings. Synthesis and properties of the molecules C, D, E and F are described in the treatise by Clar.¹⁾

Broadly speaking sandwich systems of the type contemplated here may be considered as extensions of the smaller known mono-metallocenes like ferrocene,^{2–6)} dimetallocenes like dizincocene^{7,8)} and the recently synthesised compounds of palladium⁹⁾ with $n = 3$, $R = C_7H_7^{2+}$ (cyclo-heptatiényl cation; with chlorides attached to the Pd atoms) and $n = 5$, $PAC = C_{18}H_{12}$ (tetracene cation; toluene coordinated to the apical Pd). Both synthetic compounds are composed of organometallic dications containing palladium. The tetracene compound is particularly interesting because the crystal structure shows that the five Pd atoms are not evenly distributed, being located as an irregular pentagon in one half of the sandwich and bonded through edge sites. The geometry of this compound is a departure from a majority of organo-metallics, which commonly consist of transition metal atoms connected by bridging ligands and/or coordi-

nated by aromatic and inorganic ligands.^{6,10)}

For simplicity we consider only systems which are: neutral, have identical linear or catacondensed hydrocarbon moieties, and contain a palladium middle layer. We generally impose symmetry D_{2h} in order to keep the calculations tractable. In the case of tetracene we consider $n = 4$ (linear array of Pd atoms), $n = 5$ (irregular pentagonal array, corresponding to the experimental geometry of Murahashi *et al.*⁹⁾) and $n = 9$ (to explore saturation of edge sites). The $Pd_5[C_{18}H_{12}]_2$ system provides a good test of the efficacy of the computational scheme used and we note the methodology used in this paper provides a good account of the geometrical structure of the experimental system. Space does not permit a full account of all geometric and electronic structure calculations including bonding. In this paper we concentrate on reporting geometry, pointing out emergent motifs in the chemical bonding as the hydrocarbon size or number of metal atoms is increased. Identifying bonding motifs is important because the mismatch between palladium neighbour distance 275 pm (fcc, bulk) and the aromatic ring centers (240–245 pm) implies a significant level of frustration. Supportive work not explicitly described here includes spin polarized calculations to verify that the ground states are not magnetic, and total energy of formation from calculations of the energy of separated hydrocarbons and palladium arrays and clusters. There are many configurations for a given number of metal atoms trapped between polyacenes in registry. An exhaustive search through all possible configurations has not been performed. Instead we have used intuitive guess work modified by ongoing calculations to guide the survey plus the knowledge of the experimental geometry from the “lopsided” experimental sandwich $Pd_5(C_{18}H_{12})_2$.⁹⁾

This paper is organized as follows. Next, there is a description of the computational method, in essential minimal detail. This is followed by a section on several sandwiches of tetracene. Then comes a section surveying the

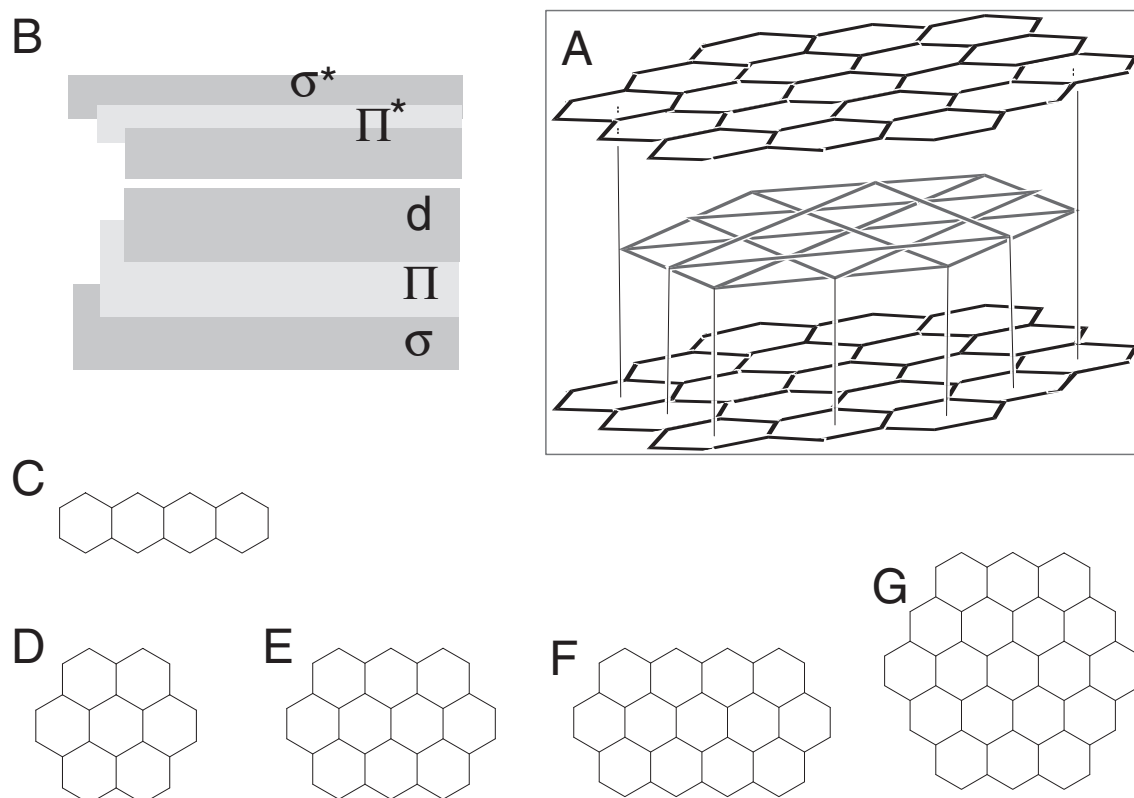


Fig. 1 Schematic diagram of the structure of metal sandwich molecules. The top right A, schematic showing a layer of metal atoms between planar aromatic molecules. Top left B, schematic of the electronic levels manifold of the sandwich subdivided into σ - and π -levels of the hydrocarbon and a 4d manifold of metal atom levels. Bottom C, D, ..., G show the carbon skeletons of the aromatic hydrocarbon molecules.

calculated geometry and bonding in sandwiches with the catacondensed polyacenes: coronene ($C_{24}H_{12}$, seven rings), ovalene ($C_{32}H_{14}$, ten rings), circumanthracene ($C_{40}H_{16}$, 13 rings), and circumcoronene ($C_{54}H_{18}$, 19 rings). The last section presents a brief summary and discussion of the bonding motifs that have been found in this study.

2. Computational Method

All calculations were performed using the Vienna *ab initio* simulation package VASP.^{11–16} The plane wave based calculations used PAW pseudo-potentials¹⁷ and the spin polarized generalized gradient approximation for the exchange-correlation energy functional parameterized by Perdew *et al.*^{11,12} The valence shell of palladium was treated as a ten electron system ($4d^85s^2$). Valence electrons were assigned as follows: Pd (10), C (4), and H (1). All calculations were performed using periodic boundaries with a cubic cell, edge lengths in the range 0.75 nm to 2.50 nm, so the molecules were at least 0.9 to 1.0 nm apart. All Brillouin zone integrations were done at the gamma point. The geometry optimizations were carried out using the conjugate gradient method usually until the forces acting on each atom were approximately ≤ 5 meV/Å. We routinely calculated geometry, total energy for given total spin, isometric surfaces of total charge, spin density and in some cases ELF. Decomposition of total charge density into partial charges based on Kohn-Sham levels was also performed in selected

cases. Harmonic analysis of the wave function inside spheres with centers on individual atoms also assisted the analysis of charge density of the chemical bonds. The starting geometries were aromatic hydrocarbons with standard bond lengths, and metal atoms located at the ring centers in many but not all cases.

3. Coordination in Sandwich Molecules

Figure 2 (a, top left) shows schematically the possible binding sites A, B, C, D of the metal atom to the hydrocarbon layer using the carbon skeleton of the linear polyacene pentacene. The coordination of carbon atoms to a metal atom in a sandwich is shown in more detail at the bottom as Fig. 2(b). The site A (η^2 -coordination) shows bonding to two adjacent C atoms in each layer. Site B (η^3 -coordination) on the circumference of a molecule has two flavours, convex (B inside) or concave (B outside). At the edge of the hydrocarbon the metal atom on a concave site would lie outside the footprint of the hydrocarbon and might be important in catalysis reactions. The site C (η^4 -coordination) involves four carbon atoms and site D (η^6 -coordination) involves coordination of the metal atom to a ring of six carbons. The quantization axis z is parallel to the metal plane (molecular L axis) and x -axis is perpendicular to the sandwich plane. In this axis system direct Pd-Pd bonding involves palladium d_{z^2} , s - and p_z -functions. The orbitals involved in Pd-C bonding are schematically shown in Fig. 2 (c, top right). Note

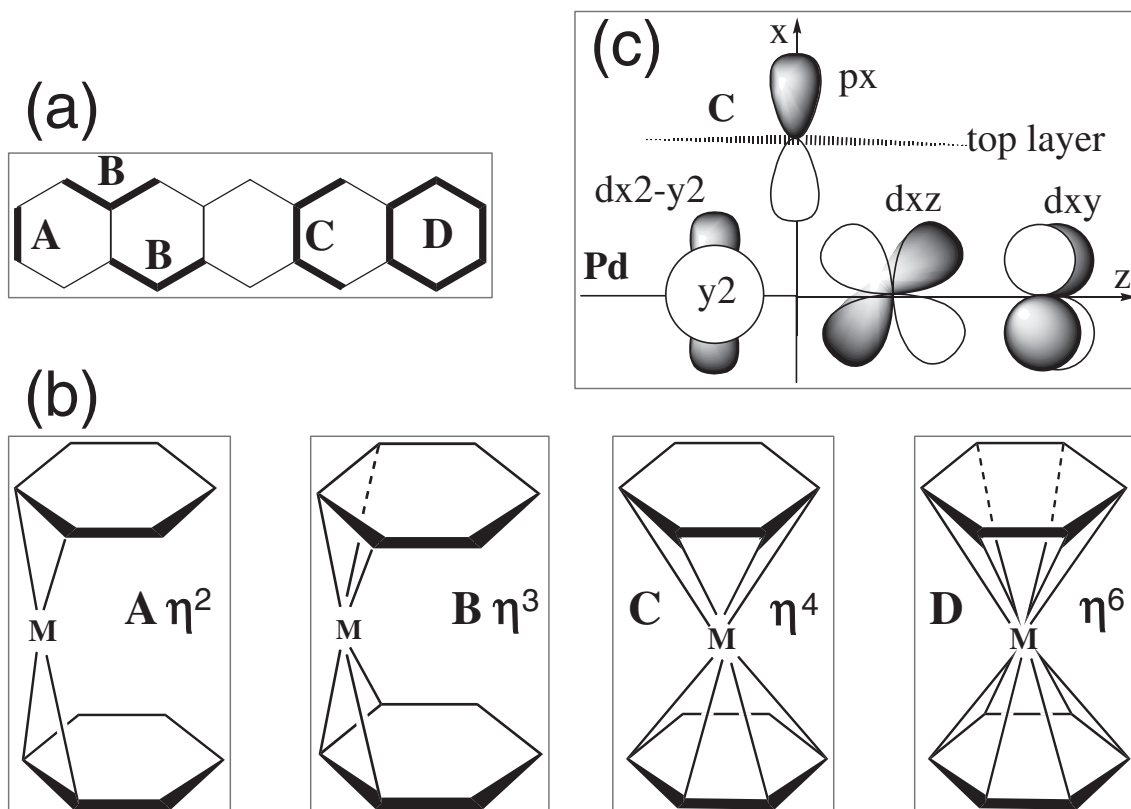


Fig. 2 Bonding sites of palladium inside the sandwich: (a) hydrocarbon bonds comprising the A-, B-, C-, D-sites; (b) position of the metal atom and the Pd-C bonds; (c) schematic of the relative orientation of metal d-orbitals and the carbon p-orbitals. Note the axis system with x-axis perpendicular and z-parallel to the hydrocarbon plane.

the orthogonal axes with x -axis perpendicular to the hydrocarbon plane and the z -axis parallel to the plane. For Pd-C bonds there are many ways the 4d orbital functions of Pd can engage the carbon π -functions (p_x - in the given geometry). Some of the orbitals involved in Pd-C bonding are schematically shown in Fig. 2 (c, top right). The y^2 -lobe of the $d_{x^2-y^2}$ -function when appropriately combined with 5s- can contribute to η^2 -bonding.

4. Sandwich Molecules $\text{Pd}_n(\text{C}_{18}\text{H}_{12})_2$ with $n = 4, 5$ and 9

Figure 3 shows top and side views of converged geometries for three sandwich complexes $\text{Pd}_n(\text{C}_{18}\text{H}_{12})_2$ where $n = 4, 5$ and 9 . The sandwich Pd_4 (Fig. 2(a)) has D_{2h} symmetry and B and C both have C_{2v} symmetry. In sandwich A the four metal atoms are confined by D_{2h} symmetry to reside on the z -axis. Sandwich B is the geometry of the Pd_5 -compound synthesized by Murahashi *et al.*⁹ The z -axis is parallel to the sandwich long (L, horizontal in the Fig. 3) axis, and x -axis is perpendicular to the hydrocarbon planes (vertical in the side view panels on the right side of Fig. 3). In this and the following Figures direct metal-metal bonds are shown only if the Pd-Pd separation is 300 pm or less. Though a 300 pm cut-off may seem high, compared to the Pd-Pd nearest neighbour distance 275 pm, it is partly supported by analysis of total charge isosurfaces showing weak bonding with central charge densities about half those found for the Pd-C edge bonds. Inspection of top and side elevations in Fig. 3 shows there is a strong preference for the metal atoms

to occupy A (η^2) and concave B (η^3) sites in a “railway” tie ($\parallel y$) configuration. There are no atoms on C (η^4) or D (η^6) sites.

4.1 $\text{Pd}_4(\text{C}_{18}\text{H}_{12})_2$ with D_{2h} symmetry

The geometry for $\text{Pd}_4(\text{C}_{18}\text{H}_{12})_2$ in D_{2h} symmetry is shown as a top and a side view in Fig. 3(a). All the metal atoms are constrained to lie on the z -axis (long axis) of the sandwich. The sites are all A-type. The metal atoms are displaced off the ring centers in opposite directions. There are two nearest metal-metal separations are Pd-Pd = 278 (connected) and 475 pm (not connected). Typical Pd-nearest C atom are 228 pm, the C atoms in opposing tetracenes are 434 pm apart when also attached to Pd atoms and 456 pm for the central C atoms. This difference results in a small buckling of the tetracene molecules. The C-H bonds at the ends of the molecule are bent away from the yz -plane so that the H-H separation parallel to the x -axis is about 463 pm. This outward tilt (approximately 9°) hints at a small hybridization change away from C (sp^2) for the C atoms attached to the Pd atoms. This geometric tilt of the C-H bonds is a common occurrence in all these sandwich molecules described here. Examination of total and partial charge densities of the Kohn-Sham levels showed that palladium d-functions overlap tetracene π^* -functions. There are many possible combinations. In the bonding at the A (η^2) sites we find that carbon C(p_x) functions overlap with palladium d_{xy} -functions and with functions in which s - and the y^2 lobe of $d_{x^2-y^2}$ are combined.

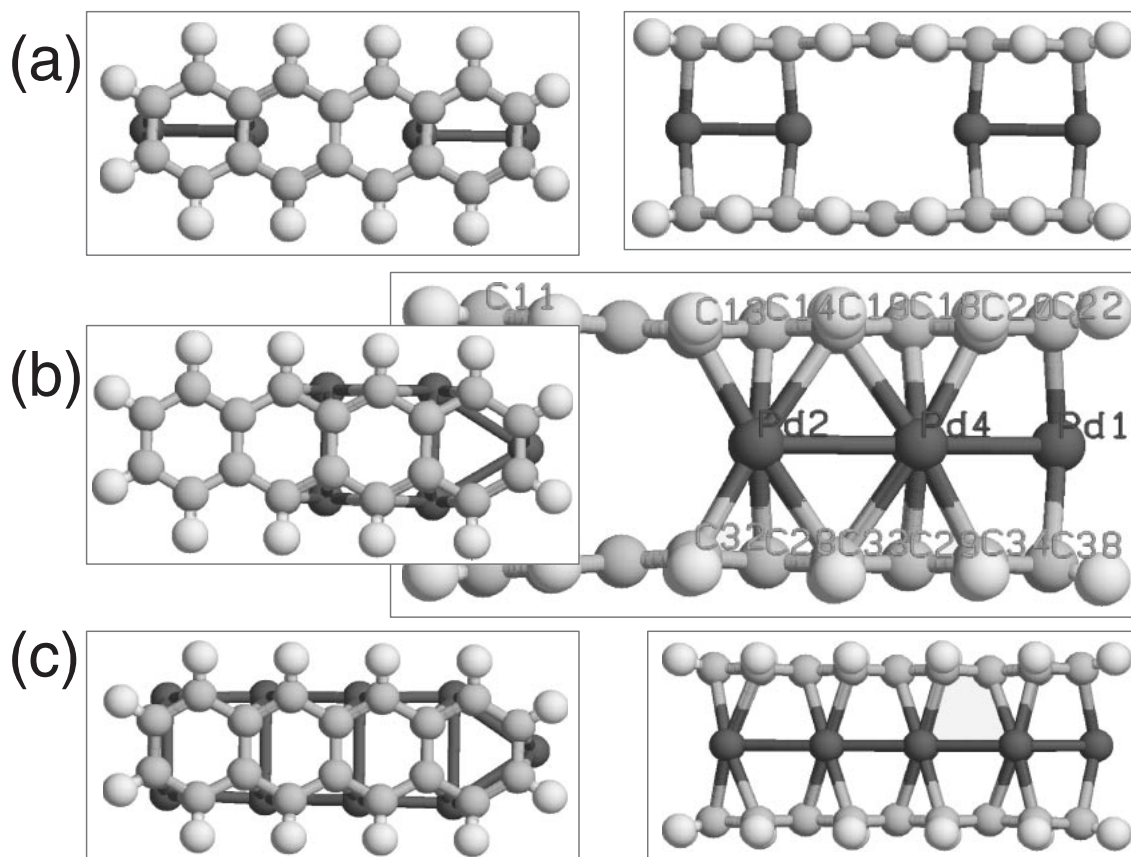


Fig. 3 Top and side views of the converged geometry of palladium sandwiches with tetracene outer layers: (a) $\text{Pd}_4(\text{C}_{18}\text{H}_{12})_2$ symmetry D_{2h} ; (b) $\text{Pd}_5(\text{C}_{18}\text{H}_{12})_2$, symmetry C_{2v} , main atoms of side view are labelled; (c) $\text{Pd}_9(\text{C}_{18}\text{H}_{12})_2$, symmetry C_{2v} .

4.2 $\text{Pd}_5(\text{C}_{18}\text{H}_{12})_2$ sandwich

In Fig. 3(b) we show the side and top view of the neutral $\text{Pd}_5(\text{C}_{18}\text{H}_{12})_2$ compound in C_{2v} symmetry. The labels on the side view are for interpreting the bond distances displayed in Table 1, which shows the main atom-atom distances from the DFT calculations and comparison with the crystal data.⁹⁾

The torsion angles between the C-H bond at terminal positions and the aromatic ring informs about the hybridization state of the C atom (for example C22 and C38 in Fig. 3(b)). We find angles of approximately 15° for the H atoms at the A-sites for the apex atom (Pd1 in Fig. 3(b)) and approximately zero angle for the C(11)-H bond at the opposite end of the molecule. Due to the contraction of the molecule around the Pd atoms, an indication of chemical bonding, the sandwich is narrower ($\parallel x$) at the end with the Pd atoms. This is clearly visible in Figure 3b where for example C22-C38 = 422 pm and C11-C41 = 466 pm.

The overall agreement between computation and experiment is good considering that important environmental effects are not included in this calculation (dication, coordination of Pd(1) atom with toluene, crystal packing, Madlung field). We find Pd(1) is on an A-site, Pd(5) is on an A-site, Pd(3) looks intermediate between A- and B-sites. Clearly the interaction between neighbouring Pd atoms has an effect here.

4.3 $\text{Pd}_9(\text{C}_{18}\text{H}_{12})_2$ sandwich

This molecule, when compared with $\text{Pd}_5(\text{C}_{18}\text{H}_{12})_2$, shows

Table 1 Geometry of the $\text{Pd}_5(\text{C}_{18}\text{H}_{12})_2$ sandwich with C_{2v} symmetry.

Atom-atom	DFT	Experiment (dication)	Comment
Pd-Pd			
Pd (1, 4) = Pd (1, 5)	284	268.7/270.0*	
Pd (4, 2) = Pd (3, 5)	285	277.9/278.1	
Pd (2, 3)	289	291.6	
Pd (4, 5)	296	277.0	
Pd-C			
Pd1-C22	222	229/230	A-site
Pd1-C23	222		
Pd4-C20	232	226/229	A- or B-site
Pd4-C18	223	219/219	
Pd4-C19	253	234/233	long
Pd2-C19	250	230/238	A- or B-site, long
Pd2-C14	218	216/218	
Pd2-C13	226	234/233	

*Two entries because of lower symmetry in the crystal.

the importance of the edge bonding motif. It has a new feature not possible in the Pd_5 -compound, namely that metal atoms can be attached in a linked pattern to a sequence of edge carbons the entire length of the hydrocarbon layers. The Fig. 3(c) shows the plan and elevation of the $\text{Pd}_9(\text{C}_{18}\text{H}_{12})_2$ geometry which is related to the previous Pd_5 -molecule by

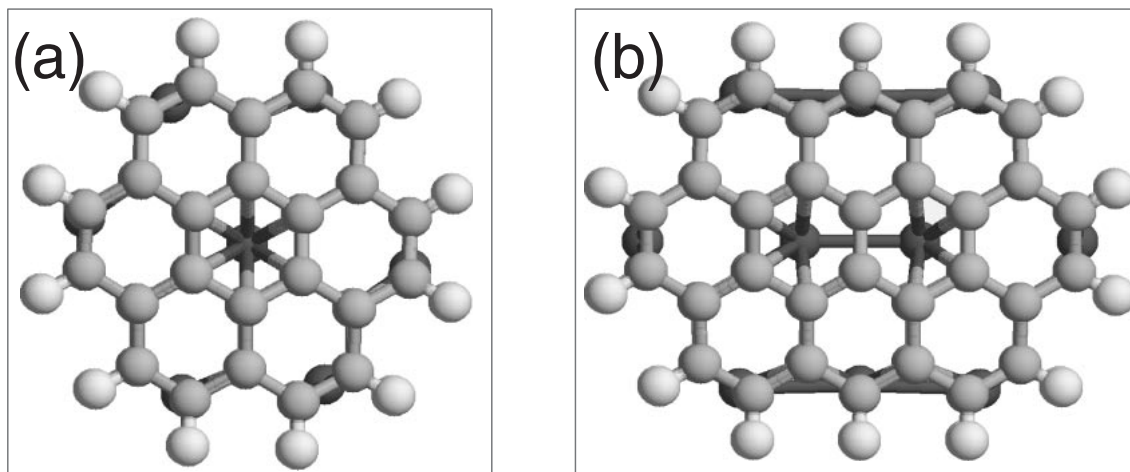


Fig. 4 Top views of the converged geometry of palladium sandwiches with coronene and ovalene in D_{2h} symmetry; (a) $\text{Pd}_7(\text{C}_{24}\text{H}_{12})_2$; (b) $\text{Pd}_{10}(\text{C}_{32}\text{H}_{14})_2$. Palladium atoms closer than 300 pm are shown connected.

adding four metal atoms in a way that forms a series of “railway ties” across the interior of the molecule. The Pd-Pd and Pd-C distances are roughly the same as those previously described. The Pd-C distances all suggest the atoms have A or B site bonding with minimum charge density along the Pd-C directions about twice that found between the metal atoms along the periphery. All the C-H bonds are tilted back out of plane as found for the apex of the Pd_5 -molecule. This suggests there is a small change in hybridization on the carbon atom consistent with incipient directed Pd-C bond formation.

Specific comments on metal-metal bonding based on distances are in order. We label the Pd atoms 1, 2, 3, . . . , 9 clockwise starting from the unique apex Pd(1) atom. Going around the periphery of the metal atoms we find: Pd(1, 2) = Pd(9, 1) = 263; Pd(2, 3) = Pd(8, 9) = 260; Pd(3, 4) = Pd(7, 8) = 260; Pd(4, 5) = Pd(6, 7) = 272; Pd(5, 6) = 266 pm. Across the Pd array the “railway tie” structures from left to right in Figure 3(c) the Pd-Pd distances are: Pd(5, 6) = 266; Pd(4, 7) = 286; Pd(3,8) = 286; Pd(2,9) = 296 pm. Note increase from “blunt to pointed end”. All are less than 300 pm and the periphery separations are comfortably close to the metal neighbour spacing to suggest metal-metal bonding. This is supported by the total charge density plots.

5. Sandwich Molecules with Coronene and Ovalene

In the coronene system $\text{Pd}_7(\text{C}_{24}\text{H}_{12})_2$, Fig. 4(a), there are palladiums at A-, B- and D-sites (η^6 -coordination). This system is interesting because unlike the systems considered so far, there is a central atom on a D-site in the sandwich interior. The Pd atoms on the edge are in A-sites and B-sites, though in the latter the metal atom is not in complete registry with the nearest C atom. This is an interesting effect which needs to be investigated further by, possibly by changing symmetry and the number of metal atoms. Symmetry in Figure 4a is D_{2h} . All the Pd-Pd distances, radial from the central atom and between edge atoms, are greater than 300 pm and so no palladium atoms are drawn linked to others. Metal-metal interactions will occur via π -states of the

hydrocarbon. The occurrence of six metal atoms on the molecular circumference opens real estate that could be occupied by additional atoms if the symmetry of the sandwich were changed, as for example by replacing the central atom by a triangular group.

The ovalene system $\text{Pd}_{10}(\text{C}_{242}\text{H}_{14})_2$, top view converged geometry is depicted in Fig. 4(b). It shows there are metal atoms on A-, B- and C-sites. The two central metal atoms with a separation Pd-Pd = 278 pm constitute an interior set, each atom being in an apparent C-site (η^4 -coordination). In addition on the long side there are groups of three peripheral Pd atoms 278 pm apart. In the total charge density these edge atoms display weak metal-metal bonding, and stronger Pd-C bonding. This system is interesting because like $\text{Pd}_9(\text{C}_{18}\text{H}_{12})_2$ it has lines of metal atoms on the edge which total charge density plots show are directly but albeit weakly coupled, a structural motif described above for the linear polyacene tetracene systems, but new for the for catacondensed polyacenes.

6. Sandwiches with Circumanthracene and Circumcoronene

In Fig. 5 we display top view geometries of sandwiches $\text{Pd}_{14}(\text{C}_{42}\text{H}_{16})_2$ and $\text{Pd}_{19}(\text{C}_{54}\text{H}_{18})_2$ the first containing circumanthracene a known molecule¹⁾ and the second hypothetical molecule circumcoronene (dodecabenzocoronene) is of some interest in graphene^{18,19)} and in astrophysical studies of interstellar carbon.²⁰⁾ Though these calculations do not have fully converged geometries they show the continuation of bonding motifs established for the smaller systems.

In the sandwich with circumanthracene Fig. 5(a), there are three interior atoms with separation of approximately Pd-Pd = 264 pm somewhat less than in the ovalene system. This linear core is further separated from the terminus palladiums on A-sites. In the direction of the y-axis the core Pd atoms are just less than 300 pm distant. This could be a new structure motif. It waits on more elaborate calculations. At the metal edge sites parallel to the long axis ($\parallel z$) the Pd-Pd distances are 266 pm (central pair) and 286 pm (out pairs). Finally we

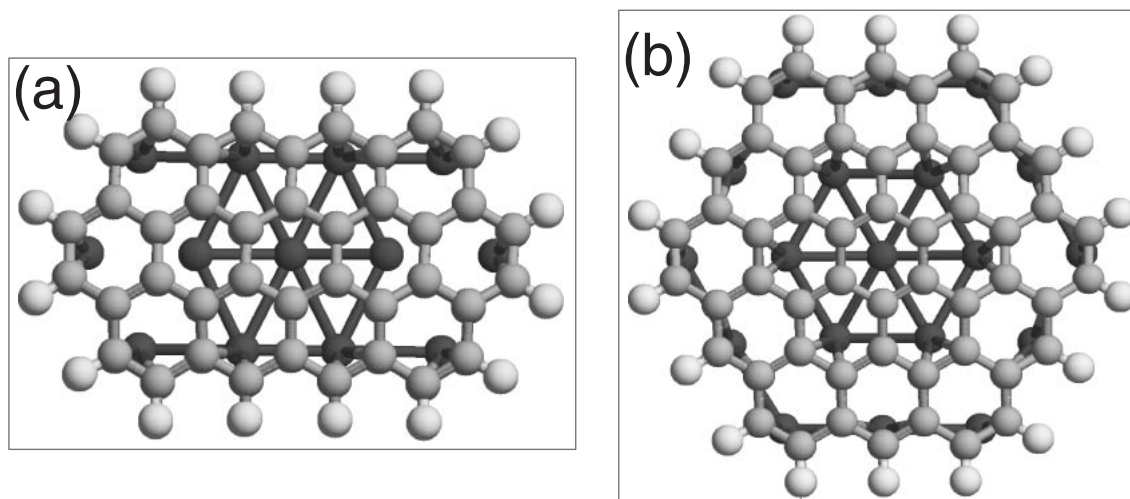


Fig. 5 Top views of the geometry of palladium sandwiches with circumanthracene and circumcoronene in D_{2h} symmetry; (a) $\text{Pd}_{13}(\text{C}_{40}\text{H}_{14})_2$; (b) $\text{Pd}_{19}(\text{C}_{54}\text{H}_{18})_2$. Palladium atoms closer than 300 pm are shown connected.

note that the aromatic hydrocarbons are not flat. There is a distinct bulge in the central region suggesting repulsion between core atoms and the hydrocarbon core to chemical Pd-C bonding at the edges.

In the sandwich with circumcoronene, Fig. 5(b), there are seven interior metal atoms and 12 attached to edge carbon atoms at A- and B-sites. Many of the Pd-Pd separations are less than 300 pm and so are represented as connected in the Figure. In the core region the mean radial Pd-Pd distance is 284 pm. The Pd-Pd distances around the hexagonal core average $\text{Pd-Pd} = 284$ pm implying weak direct bonding amongst the Pd core. This conclusion receives support from the total charge density distribution. Metal-metal separations around the edge are quite sensitive to distance from the center. About two thirds are less than 300 pm and the rest slightly greater. Accordingly it is an open question as to whether the edge atoms are directly bonded. There is some support from total charge density isosurfaces which show joining at a charge density about one half of that for the Pd-C bonds.

7. Discussion and Summary

In this report we have identified structural motifs that relate to palladium atoms binding at edge and interior sites. Though the focus was on geometry we have studied, but not reported here, the stability of the sandwich compounds with respect to disproportionation. Briefly, we find the systems are energetically stable compared to separated hydrocarbons and the most stable metal cluster or separate atoms for a given palladium number n . This preliminary finding is of interest because it has been found that on fullerene surfaces some metal atoms prefer to cluster.²¹⁾

Edge sites were identified as A (η^2 -) and B (η^3 -coordination). Interior sites additionally included C (η^4 -) and D (η^6 -coordination). The Pd-C bonding was found to be more localized and have higher charge densities (factor $\times 2$) than Pd-Pd bonds where the latter were found. More needs to be done, especially regarding varying both the symmetry and the number of metal atoms involved, and examining individual

Kohn-Sham level components of the electron density. The C-sites can shift into A-sites and D-sites and so may be artifacts of the assumed symmetry. Another problem unexplored here is the cross metal registration of the hydrocarbon moieties. Because edge state effects appear strongly in the smaller polyacenes and higher palladium n values will be needed before an interior metal array occurs. The interaction of an interior array with edge atoms is of interest for many reasons. This connection to metal intercalated graphite²²⁾ is an interesting area for future research.

There has been a lot of interest in polycyclic aromatic hydrocarbons as models for graphene, and single walled nanotube surfaces and as interstellar reservoirs of carbon.²⁰⁾ The rational organo-metallic synthesis of sandwich systems may prove extremely arduous. However we note that alternative routes involving epitaxy may arise following recent progress in building graphene structures.^{18,19)} The molecules described in this report would have potential applications in nano-electronics. Long narrow sandwiches could provide function in connectors or in sensors and compact sandwiches could provide function as capacitors or chemical batteries. Sandwiches may provide tractable models for site geometry and over potential characteristics of surface edge sites where metal transfer in and out of intercalation states occurs.

In this work we have reported only spin paired calculations. It is known that palladium clusters are only weakly magnetic²³⁾ and in this study we find that all the ground electronic states are non-magnetic (spin $S = 0$). This has been checked by calculating the energy and geometry of the lowest triplet state $S = 1$. In the cases examined we found the magnetic states to be higher in energy. This state of affairs does not apply to atoms such as iron or chromium, where in preliminary calculations we found spin polarized ground states.

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