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DFT Modeling of Sandwich Complexes Involving Cationic Palladium Chains and Polyenic or Polycyclic Aromatic Hydrocarbons

Pierre Labéguerie, Marc Bénard,* and Marie-Madeleine Rohmer

Contribution from the Laboratoire de Chimie Quantique, Institut de Chimie, LC3-UMR 7177, CNRS-ULP, Strasbourg, France

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DFT calculations are reported on a series of one-dimensional palladium complexes with general formula $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$ ($m = 2$–4, $n = 2$–8, $n \geq m$), in order to model and analyze the bonding in the series of organometallic sandwich compounds recently reported by the group of T. Murahashi and H. Kurosawa. The bonding interactions are elucidated, and the frontier orbitals involved are described as a function of the haptotropic conformation of the metal atoms, either di-hapto or tri-hapto. In both cases, the driving force to the complex organization is a strong donation interaction from the π system of the hydrocarbons to an orbital with appropriate phase and composition, delocalized over the metal chain, and depopulated by the double oxidation process. No net bonding interaction can be characterized along the metal string, and the metal–metal distances are mainly governed by the hapticities of adjacent atoms. The energy associated with the formation of a complex is calculated with respect to its fragments, assumed either isolated or solvated. The results emphasize the stabilizing role of a large delocalization of the positive charge transferred to the hydrocarbons. This delocalization extends to the hydrocarbon regions not directly in contact with palladium and highlights the importance of these “inactive” regions in complexes made from diphenyl polyenes or polycyclic aromatic hydrocarbons. Finally, the bonding pattern deduced from calculations has been utilized to consider the feasibility of novel sandwich architectures, whose computed energy balance eventually proves similar to that of already existing compounds.

1. Introduction

A new class of complexes, made of dicationic chains of palladium atoms intercalated between unsaturated hydrocarbons, either polyenic or polybenzenic, has been developed since 1999 by Murahashi, Kurosawa et al.[1−10] This family of compounds lies at the crossing point between two very active research domains in the field of organometallic chemistry: sandwich complexes, which are widely used in the fields of molecular materials and catalysis,[11] and extended metal atom chains,[12−14] developed in view of their potential applications as molecular wires and switches in nanoelectronics.[13−15] Even though DFT calculations were recently

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* To whom correspondence should be addressed. E-mail: benard@quantix.u-strasbg.fr.

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reported to explain the stabilization of a planar $(Pd_5)^{2+}$ cluster sandwiched by two tetracene molecules,[9] no theoretical model has been proposed to date for delineating the respective roles of the metal−metal and of the metal−ligand interactions in the formation of such complexes and in the observed growth of palladium chains templated by diphenyl polyenes.[1,3,6] We report a series of investigations carried out at the density functional theory (DFT) level on model complexes of dicationic chains of 2, 3, and 4 palladium atoms sandwiched by linear polyenes of variable length. The relative stabilities of the sandwich complexes with respect to their isolated fragments are discussed as a function of various factors such as the number of metal atoms, the length of the polyene ligands, the axial coordination of the metal chain, the haptotropic variants of the coordination, and the solvent accessibility. The perylene−tetrapalladium sandwich complex reported by Murahashi et al.[5] was also investigated and we eventually discuss the possibility to use polycyclic aromatic hydrocarbons (PAHs) for stabilizing *cyclic* clusters of palladium atoms.

2. Models for $[Pd_n]^{2+}$-Polyene Complexes and Computational Details

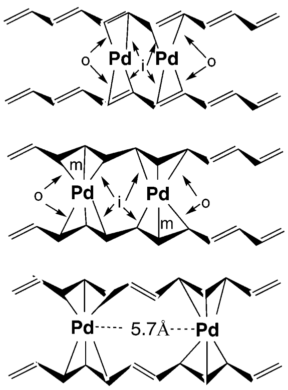
Calculations have been carried out on dicationic chains of palladium atoms sandwiched between two linear polyenes with variable length. Except when specified, the polyenes are in the all-trans conformation, and the relative conformation of two polyene ligands is eclipsed (meso isomer).[4] The general formula of the model complexes is therefore $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$, with $n \geq m$. This is indeed at variance with the real polypalladium chain complexes, which have been characterized to date with *diphenyl-polyene* ligands, the phenyl substituents either taking part in the bonding with palladium,[1,6] or just being spectators.[1,3,7] The choice of plain polyene model ligands was made in order to more easily delineate the contribution of single factors such as n and m to the bond energy and also because of the well-documented difficulty to adequately account at the DFT level for the π-stacking energy between phenyl rings. The stabilization energy for one polyene, $\Delta E^{\eta}_{n,m}$, where η represents the hapticity, is calculated with respect to the polyene and metal fragments separately optimized:

$$\Delta E^{\eta}_{n,m} = -\frac{\mathbf{E}[Pd_m(C_{2n}H_{2n+2})_2]^{2+} - 2\mathbf{E}(C_{2n}H_{2n+2}) - \mathbf{E}[Pd_m]^{2+}}{2} \qquad (1)$$

The electronic conformation of the oxidized metal chain $[Pd_m]^{2+}$ was assumed to be the closed-shell, σ-bonded state with the σ^* orbital highest in energy left unoccupied.

All calculations have been carried out within the framework of DFT, using the 2004 version of the ADF program[16] with the gradient-corrected BP86 exchange−correlation functional.[17] This GGA functional is of general use and known to provide accurate equilibrium geometries and energy differences, as far as the compared electronic configurations belong to the same spin multiplicity. All atoms are described with the Slater basis sets referred to as TZP in the user's guide. The basis set for hydrogen is triple-ζ plus one p-type orbital. For carbon and nitrogen atoms, the 1s core is frozen and described by a single Slater function, whereas the valence set is triple-ζ and supplemented with a d-type polarization function. The small core (3s3p3d) of palladium was also modeled by a frozen Slater basis. The valence shell is double-ζ for 4s, triple-ζ for 4p, 4d, and 5s, and supplemented with a single Slater orbital describing the 5p shell. These basis sets have been used in conjunction with the zero-order regular approximation (ZORA)[18] to the relativistic effects. Geometry optimization on all model compounds involving the $[Pd_2]^{2+}$ metal and on several systems with a larger metal framework have also been carried out in the presence of the conductorlike screening model (COSMO)[19] which accounts for the solvent effects (water, $\epsilon = 78$).

Scheme 1



3. Haptotropic Conformations

A metal atom bonded to an unsaturated hydrocarbon, either conjugated or aromatic, can adapt its coordination environment to the steric or electronic constraints by slightly shifting its position with respect to the ligand backbone, modifying the number of actually coordinated atoms. In the present $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$ complexes, each palladium atom has in principle the choice between two conformations: (i) a *di-hapto* conformation, in which the metal is coordinated up and down to two carbon atoms formally corresponding to a double bond in the bond alternation pattern (Scheme 1, top), and (ii) a *tri-hapto* conformation, in which the metal is globally coordinated to six carbon atoms (Scheme 1, middle and bottom). These coordination modes give rise to four "outer" (o) Pd−C bonds, four "inner" (i) bonds, and for the tri-hapto conformation, to four intermediate (middle, m) bonds (Scheme 1). The di-hapto coordination does not modify the bond alternation scheme, so that the position of a sandwiched metal chain can be easily shifted along the coordinated hydrocarbons. At variance with the former case, the tri-hapto coordination interrupts the sequence of short and long C−C bonds, and the sections of the hydrocarbons not affected by coordination should be able to reorganize according to a polyenic bond alternation scheme (Scheme 1).

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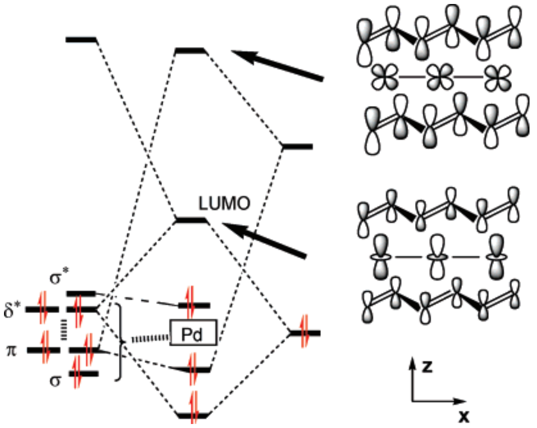

Figure 1. Qualitative orbital interaction diagram for a $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$ complex in which all metal atoms adopt a di-hapto coordination mode. Note that in electron-rich complexes such as those involving palladium, the orbitals with metal contribution most easily schematized and analyzed are *unoccupied*. The intermetallic interactions occurring in those MOs provide an inverse image of the metal−metal bonding in the complex.

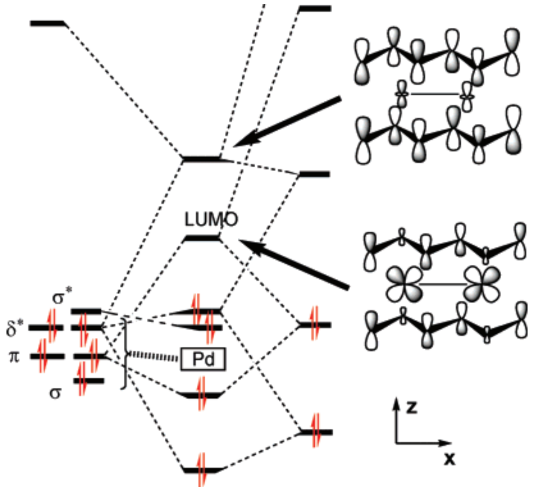

Figure 2. Orbital interaction diagram for a $[Pd_2(C_6H_8)_2]^{2+}$ complex with the two metal atoms in a tri-hapto coordination mode. See comment in Figure 1.

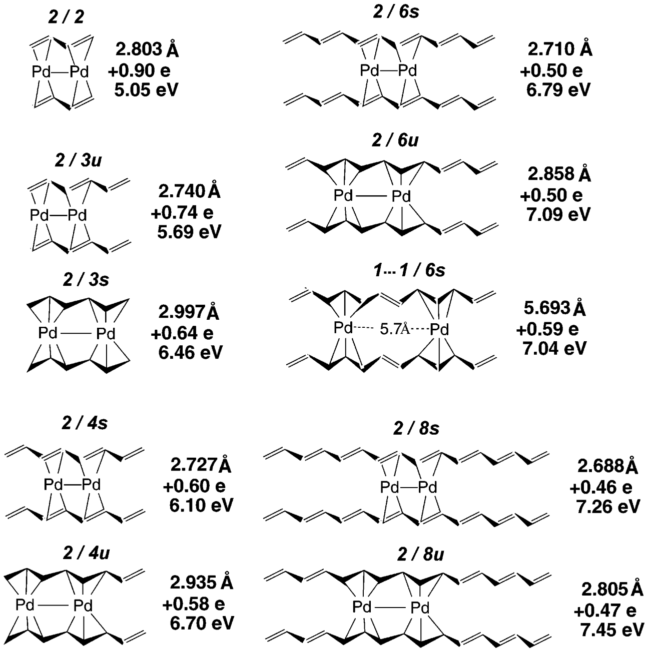

Figure 3. Results of DFT calculations carried out on a series of $[Pd_2(C_{2n}H_{2n+2})_2]^{2+}$ complexes, labeled as 2/*nx* (*x* = s, symmetrical; u, unsymmetrical): optimized Pd−Pd distance (Å); Mulliken charge of the metal framework (electrons); stabilization energy with respect to fragments (eV).

The orbital interaction schemes typical of the di-hapto and tri-hapto coordination modes in a sandwiched dicationic metal chain are displayed in Figures 1 and 2, respectively. In both cases, stabilization is obtained by means of a major donation interaction, completed with a minor back-donation interaction, but the metal orbitals involved in these interactions are interchanged in the two coordination modes. In the di-hapto mode, the donation occurs toward a d_{z^2}-like metal orbital combination, which becomes the major component of the LUMO. The back-donation stabilizes an orbital combination with metal−metal π-bonding character (Figure 1). The role of these two metal orbitals is reversed in the tri-hapto mode: the *donation* interaction destabilizes the metal−metal π-bonding orbital, which becomes the LUMO, whereas the back-donation interaction stabilizes the d_{z^2}-like metal MO (Figure 2). It is interesting to consider these interaction diagrams from the point of view of the metal−metal bonding. Let us assume first that the contribution of the back-donation interaction is negligible. The character of the interaction delocalized along the metal−metal chain can therefore be described as the mirror image of the metal contribution to the LUMO. In the di-hapto conformation, this interaction appears formally bonding, but it is clear that the d_{z^2}-like metal MOs generate a very weak, mainly δ-type overlap along the metal chain. The back-donation interaction generates an unoccupied orbital with metal π-bonding character (Figure 1), which means that the contribution of this interaction with respect to the metal chain is antibonding and probably sufficient to annihilate most of the Pd−Pd bonding character (Figure 1). In the tri-hapto conformation, the metal contribution to the LUMO is π-bonding, which implies that the major metal−metal interaction is globally *antibonding* (Figure 2). Note, however, that a direct contact between two Pd atoms in a tri-hapto conformation has been calculated and observed only in dipalladium sandwich complexes (Figure 3). In longer metal chains, only the terminal atoms adopt the tri-hapto conformation (Figures 4 and 5). The hapticity, η, associated with a sandwiched Pd framework will be referred to as the sequence of the coordination numbers of the metal atoms with respect to one polyene.

As in most transition metal complexes, an important and isotropic donation also occurs toward the 5s and 5p shells of palladium and contributes to stabilize the sandwich coordination. In order to roughly apprehend the role of this contribution, we optimized the structure of a hypothetic *neutral* $Pd_2(C_4H_6)_2$ complex, with η = (2, 2). The Pd−Pd distance increases to 3.00 Å, whereas the Pd−C bonds are shortened by 0.08 and 0.10 Å with respect to the dication. This contraction of the structure results from the vanishing of the intramolecular electrostatic repulsion. In spite of this apparent strengthening of the metal−ligand bond, the bond energy, ΔE, computed between the metal core and each polyene has receded from 5.05 eV in the dication (Table 1) to 2.51 eV in the neutral complex. Moreover, the overall

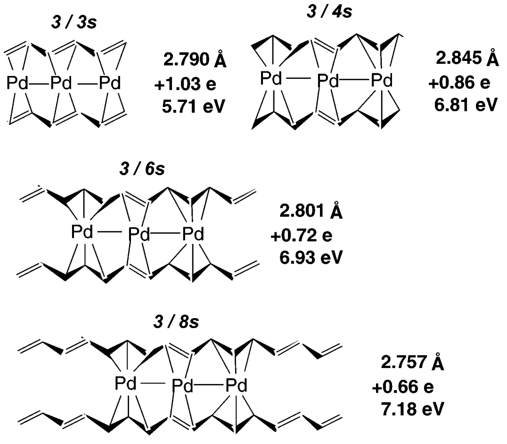

Figure 4. Results of DFT calculations carried out on a series of $[Pd_3(C_{2n}H_{2n+2})_2]^{2+}$ complexes; labels and detail of results as in Figure 3.

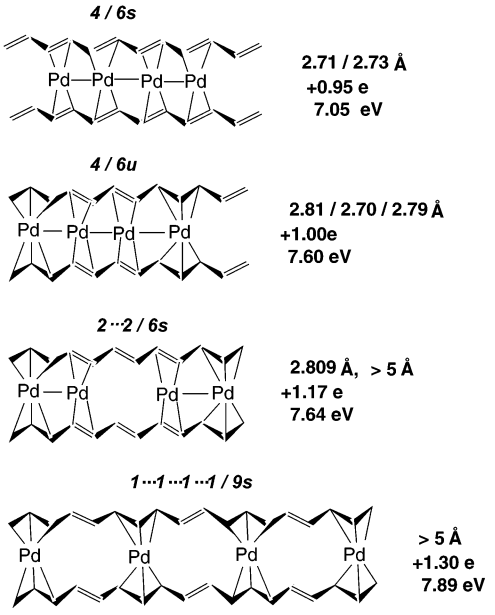

Figure 5. Results of DFT calculations carried out on a series of $[Pd_4(C_{2n}H_{2n+2})_2]^{2+}$ complexes; labels and detail of results as in Figure 3.

charge transfer has been dramatically reversed to the advantage of back-donation, now originating in both the π- and the d_{z^2}-like metal orbitals, and resulting in a *negative* population of the ligands (−0.39e for each polyene, compared to +0.55e in the dication). This calculation therefore confirms the critical importance of oxidizing the palladium framework, as far as the nature and the strength of the metal−polyene interaction are concerned.[20]

The analysis of frontier orbitals suggests that metal−metal bonding provides a minor contribution, if any, to the energetic balance of the dicationic complexes. Even though the Pd−Pd distances, either observed or computed, are in the bonding range, it appears that they are mainly governed by the interactions with the ligands. The relatively short range of the distances between di-hapto Pd atoms (2.64−2.75 Å) follows the sequence of the "short" C−C bonds in the polyenes, whereas the longer distances obtained between tri-hapto coordinated metals (2.80−3.00 Å) account for the shift requested by the extension of the coordination sphere to an outward carbon. Calculations indeed show that, provided that the host polyenes are long enough, separate Pd atoms or Pd dimers scattered along the polyenes could reasonably compete with a single palladium chain (Figures 3 and 5). The bonding mode in dicationic sandwich complexes therefore appears strongly at variance with that of platinum or iridium blues, in which an oxidation process concatenates dinuclear fragments into an unsupported chain in which metal atoms are held together by means of a strong bonding interaction delocalized along the metal framework.[21]

4. Results and Analysis of Bonding Energies

4.1. Results. The result of DFT calculations carried out on $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$ with $m = 2-4$ and various values of n comprised between m and 9 are displayed in Figures 3−5. Environment effects are not taken into account in these calculations. The hapticity of each Pd atom is indicated and each equilibrium conformation is characterized by three parameters: the metal−metal distance(s); the Mulliken charge of the metal framework, which provides an estimate for the relative strength of the donation interaction; and the stabilization energy for one polyene, $\Delta E^{\eta}_{n,m}$, as defined in eq 1.

4.2. Calculated Trends for $m = 2$ and Charge Delocalization along the Ligand π Framework. Figure 3 provides a comprehensive overview of the bonding between a dicationic Pd dimer and polyenes of variable lengths. Whatever $n > 2$, two conformations associated with distinct energy minima could be characterized, corresponding to the hapticities $\eta = (2, 2)$ and (3, 3), respectively (Figure 3). The following inferences can be made.

1. The bond energy increases with n for both types of hapticity. The same is true for the strength of the donation, deduced from the residual charge on the Pd_2 fragment.

2. The palladium dimer prefers the (3, 3) hapticity for all values of $n > 2$. However, the difference in bond energies and donation strengths reduces as n increases. An analysis of the Pd−C distances associated with the tri-hapto coordination shows that the metal atoms deeply buried into the polyenic channel hardly achieve bond formation with a third carbon atom due to the rigidity of the polyenic framework. The third Pd−C distance then becomes close to or larger than 2.5 Å unless the carbon atom is terminal (Table 1). The coordination therefore tends to become di-hapto. Even though no specific energy minimum was ever found corresponding to a mixed $\eta = (2, 3)$ haptotropic conformation, the case of a $[Pd_2]^{2+}$ dimer *asymmetrically* sandwiched between two long polyenes could approach such a conformation, as for $[Pd_2(C_8H_{10})_2]^{2+}$, computed assuming $\eta = (3, 3)$ (Table 1).

3. The Pd−Pd distance decreases as n increases for both values of η, and for a given value of n, the metal−metal separation is always larger for $\eta = (3, 3)$. The calculated

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(20) We thank a reviewer for suggesting this calculation. Note, however, that, at variance with the case of the dicationic complex, both the metal−polyene bond energy, ΔE, and the charge distribution remain practically unaffected by solvation.

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Table 1. Stabilization Energy Associated with One Polyene (ΔE, eV), Mulliken Charge of the Metal Framework [$q(Pd_m)$, Electrons], Metal−Metal and Metal−Carbon Distances (Å) for Some $[Pd_2(C_{2n}H_{2n+2})_2]^{2+}$ Complexes and for $[Pd_4(C_{12}H_{14})_2]^{2+}$ with Different Hapticities[a]

	ΔE (eV)		$q(Pd_m)$		Pd−Pd		Pd−C(o)[b]		Pd−C (i/m)[b]		Pd−C (i)[b]	
$[Pd_2(C_{2n}H_{2n+2})^{2+}$ ($\eta_{2,2}$)												
$n = 2$	5.05	*2.28*	0.90	*1.51*	2.80	*2.85*	2.24	*2.18*	2.33	*2.31*		
$n = 3$	5.69	*2.35*	0.74	*1.24*	2.74	*2.80*	2.34[c]	*2.25*	2.22	*2.25*		
							2.20[c]	*2.17*	2.35	*2.33*		
$n = 4$	6.10	*2.36*	0.60	*1.03*	2.73	*2.79*	2.26	*2.22*	2.27	*2.28*		
$n = 6$	6.79	*2.56*	0.50	*0.85*	2.71	*2.76*	2.27	*2.22*	2.25	*2.28*		
$n = 8$	7.26	*2.69*	0.46	*0.77*	2.69	*2.76*	2.27	*2.23*	2.24	*2.26*		
$[Pd_2(C_{2n}H_{2n+2})_2]^{2+}$ ($\eta_{3,3}$)												
$n = 3$	6.46	*3.08*	0.64	*1.07*	3.00	*2.98*	2.28	*2.25*	2.20	*2.18*	2.29	*2.28*
$n = 4$	6.70	*3.00*	0.59	*0.93*	2.94	*2.95*	2.62[c]	*2.47*	2.23	*2.24*	2.23	*2.25*
							2.27[c]	*2.25*	2.19	*2.18*	2.30	*2.28*
$n = 6$	7.09	*2.92*	0.50	*0.77*	2.86	*2.91*	2.71[c]	*2.60*	2.24	*2.22*	2.21	*2.23*
							2.49[c]	*2.42*	2.21	*2.19*	2.26	*2.26*
$n = 8$	7.45	*2.92*	0.47	*0.73*	2.81	*2.92*	2.82[c]	*2.69*	2.25	*2.23*	2.19	*2.21*
							2.70[c]	*2.52*	2.24	*2.20*	2.23	*2.26*
$[Pd_3(C_{12}H_{14})_2]^{2+}$ ($\eta_{3,2,3}$)[e]	6.93	*3.77*	0.72	*1.11*	2.80	*2.84*	2.49	*2.39*	2.18	*2.19*	2.29	*2.29*
$[Pd_4(C_{12}H_{14})_2]^{2+}$ ($\eta_{2,2,2,2}$)	7.05	*4.49*	0.95	*1.43*	2.72[d]	*2.74*[d]	2.20	*2.20*	2.35	*2.36*		
$[Pd_4(C_{12}H_{14})_2]^{2+}$ ($\eta_{3,2,2,3}$)[e]	7.60	*5.06*	1.00	*1.43*	2.80[f]	*2.82*	2.45[c]	*2.36*	2.20	*2.18*	2.29	*2.32*
					2.70[g]	*2.73*	2.24[c]	*2.23*	2.17	*2.17*	2.34	*2.34*

[a] In roman, results for the complex in the gas phase; in italics, results for the solvated molecule. [b] o and i refer to the outermost and innermost Pd−C bonds, respectively. In the case of tri-hapto coordination, m refers to the intermediate Pd−C bond (Scheme 1). [c] When the metal framework occupies a nonsymmetric position, the first series of Pd−C distances refers to the metal atom most inside the complex. [d] Average value. [e] The Pd−C bond lengths refer to the tri-hapto (terminal) metal atoms only. [f] Terminal Pd−Pd bond lengths. [g] Central Pd−Pd bond length.

difference amounts 0.26 Å for $n = 3$ but steadily decreases up to 0.12 Å for $n = 8$.

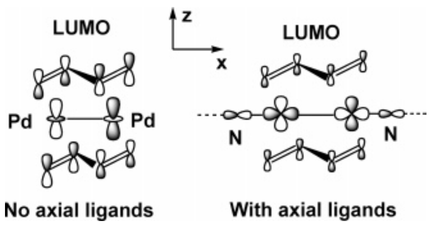
The trends concerning the bond energy and the donation strength can be correlated with a marked tendency for the polyenes to delocalize the positive charge gained from donation along all carbon atoms not involved in bonding with palladium, except for the terminal carbons. Taking the example of $[Pd_2(C_{12}H_{14})_2]^{2+}$ with $\eta = (2, 2)$, the positive charge of each polyene is +0.75e, distributed among the four CH groups involved in bonding with palladium (average charge +0.033e), the terminal CH_2 groups (+0.038e), and the six remaining CH groups (average charge +0.090e). It is clear that the donation interaction is hindered when there is little or no possibility for such delocalization, as in $[Pd_2(C_4H_6)_2]^{2+}$, for which the positive charge on butadiene is +0.55e only. Note that the efficiency of this charge delocalization is similar on the phenyl substituents of $\{Pd_m[(C_6H_5)_2C_{2n}H_{2n}]_2\}^{2+}$. A Pd_2 dication sandwiched between two diphenyl hexatrienes in eclipsed conformation ($m = 2$; $n = 3$, $\eta = 3, 3$) undergoes a global transfer of 1.53e to the metal atoms, same as in the $[Pd_2(C_{16}H_{18})_2]^{2+}$ model system, with a computed stabilization energy almost as large (7.22 eV, instead of 7.45 eV). Phenyl substituents are present in most polyene-based sandwich compounds of this family. Whatever their participation in the bonding, actors in the coordination process or just spectators, their role as powerful and compact charge reservoirs provides a major contribution to the molecular stability.

One can also notice that the important participation of *all carbon atoms* to the LUMO—which represents the counterpart to the donation interaction—ensures a delocalized interaction along the metal framework *via the ligands* and facilitates the distribution of the formal positive charge among the metal atoms, in spite of the weakness of direct, through-space interactions. The energetically favorable dissociation of a sandwiched $(Pd_4)^{2+}$ chain into two separate dimers (symmetric form of $[Pd_4(C_{12}H_{14})_2]^{2+}$, Figure 5), or into four separate atoms with (3,3) hapticipies ($[Pd_4(C_{18}H_{20})_2]^{2+}$, Figure 5) evidence the efficiency of this ligand-mediated delocalized interaction.

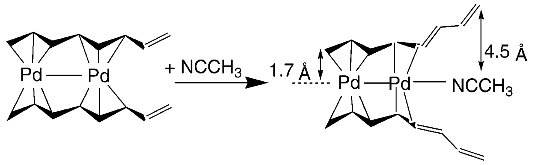
4.3. Influence of Axial Coordination. In some of the complexes characterized experimentally, the metal chain is completed in axial position by $NCCH_3$ ligands. This coordination is conditioned by steric and electronic factors, which are the accessibility of the metal chain and the hapticity of the metal atoms in the terminal position, respectively. Even though the formal electronic environment of individual metal atoms cannot be defined unambiguously due to the weakness of the intermetallic interaction and to the fractional oxidation state for $m > 2$, it is clear that tri-hapto Pd atoms in terminal position are close to electronic saturation, whereas terminal metals in di-hapto coordination are unsaturated and can accommodate an extra ligand.

This is confirmed by calculations on $[Pd_2(C_{2n}H_{2n+2})_2]^{2+}$ ($n = 2, 3$). Adding two $NCCH_3$ molecules to the butadiene complex for which $\eta = (2, 2)$ results in an effective coordination of the acetonitriles with an important elongation of the Pd−Pd distance to 3.08 Å, a Pd−N distance of 2.06 Å, and an extra stabilization of 2.13 eV for each Pd−N bond. By contrast, $NCCH_3$ does not bind to palladium in $[Pd_2(C_6H_8)_2]^{2+}$ ($\eta = 3, 3$) where the calculated metal-nitrogen distance is 4.40 Å. Note that the LUMO of the complex with outermost metals in di-hapto conformation, although belonging to the appropriate irreducible representation of the C_{2h} point group, is not properly conditioned to receive σ donation from axial ligands (Figure 1). The nature of the metal contribution is therefore modified to acquire some x^2-z^2 character at the expense of the donation from the hydrocarbons (Scheme 2). Some π contributions to the Pd−N bonds occur from back-donation involving palladium d_{xy} and d_{xz} MO combinations and the appropriate $N\equiv C$ π^* orbitals. When the axial ligand is a pyridine-like system, this back-

Scheme 2



Scheme 3



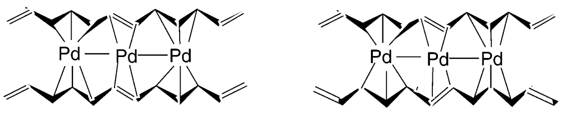
donation can be delocalized over the conjugated system and contributes to enhance a Pd═N double-bond character.

An unexpected result was obtained when attempting to bind two $NCCH_3$ molecules to $[Pd_2(C_8H_{10})_2]^{2+}$. In this model complex, the most stable form corresponds to a nonsymmetric structure in which both metals are in a tri-hapto conformation and one C−C double bond in each polyene is dangling (Pd−Pd = 2.935 Å, $\Delta E = 6.70$ eV, Figure 3). Two acetonitrile molecules added on both sides of this unsymmetrical complex behave quite differently. Only one $NCCH_3$ binds the dipalladium framework (Pd−N = 2.18 Å), after approaching the complex on the side of the dangling C═C bonds and opening like a zipper the interval between the two polyenes. Concurrently, the hapticity of the bonded palladium decreases from 3 to 2 (Scheme 3). On the opposite side, the other acetonitrile remains nonbonding (Pd−N > 4 Å), except for a weak interaction with the terminal hydrogens of the positively charged polyenes. The extra stabilization due to acetonitriles amounts 2.52 eV. Interestingly, such a zipperlike opening of the diphenylpolyene chain was observed at both sides of $\{Pd_4[(C_6H_5)_2C_8H_8]_2\}^{2+}$ upon axial coordination of pyridine.[1]

4.4. Effect of the Environment. The account of environment effects by means of the COSMO model appreciably modifies the results obtained with the free molecules, concerning the stabilization energies, the charge donation, the metal−carbon distances in the tri-hapto conformations, and more important, the evolution of these quantities with the length of the polyenes and of the metal chains. Table 1 compares these quantities for $[Pd_2(C_{2n}H_{2n+2})_2]^{2+}$ for different values of n and for $\eta = (2, 2)$ and (3, 3). The same comparison is extended to $[Pd_3(C_{12}H_{14})_2]^{2+}$ ($\eta =$[3, 2, 3]) and to $[Pd_4(C_{12}H_{14})_2]^{2+}$ ($\eta =$[2, 2, 2, 2] and [3, 2, 2, 3]).

First, the stabilization energy ΔE calculated from eq 1 is much reduced with COSMO, as an obvious consequence of the large stabilization by the solvent of the $[Pd_m]^{2+}$ fragment. However, this stabilization of the metal framework is reduced when m increases due to the dilution of the positive charge along the metal chain. The length of the polyene ligand, n, being constant, ΔE therefore *increases* with the number m of metal atoms, a trend that was not at all clear in the gas-phase results. For $n = 6$ and with a tri-hapto bonding mode of the terminal metals, $\Delta E_{\mathrm{solvated}}$ is computed to be 2.9, 3.8, and 5.1 eV for $m = 2$, 3, and 4, respectively. Without solvation, the corresponding values are 7.1, 6.9, and 7.6 eV (Table 1). The observed growth of metal chains with up to 4 or 5 Pd atoms sandwiched between diphenyl polyenes[6,8] could therefore be induced by solvation or crystal forces.

Scheme 4



meso (eclipsed) rac (staggered)

Conversely, the influence of the polyene length, which strongly contributes to increase ΔE in the free complexes, has roughly vanished with COSMO (Table 1). This should be assigned mainly to the severe competition between the solvent and the hydrocarbons for the positive charge. The formation of strong metal−solvent stabilizing interactions indeed requires the permanence of a large positive charge on the palladium framework *at the expense of the charge transfer to the hydrocarbons.* This explains why this charge transfer is *significantly reduced* with COSMO (Table 1). It is also evident that the accessibility of solvent to the metal framework is reduced by long hydrocarbon tails. Concerning this point, an optimal stability should result from the possibility to delocalize the transferred charge toward conjugated ligand ends that are compact enough to leave the metal framework accessible to solvent or to counterions. The phenyl substituents or PAHs such as perylene[5] could play this role.

It finally appears that solvation contributes to stabilize the tri-hapto conformation of the Pd atoms at both ends of the metal chain. Indeed, the geometrical changes induced by solvation remain limited, *except for the very long Pd−C distances obtained in the case of a tri-hapto coordination when* $n \gg m$. COSMO reduces these distances by 0.07−0.18 Å, making the polyene chain more flexible (Table 1). These trends summarized in Table 1 are in keeping with the structure observed for $\{Pd_2[(C_6H_5)_2C_6H_6]_2\}^{2+}$, which displays a Pd−Pd distance of 2.9156 Å and a η^3/η^3 coordination mode with each outermost Pd−C bond (2.36−2.38 Å) remaining distinctly longer than the other ones (2.17−2.23 Å).[7]

4.5. Meso/Rac Isomerism. The preparation of the $\{Pd_3[(R\text{-}C_6H_4)_2C_8H_8]_2\}^{2+}$ diphenyltetraene complex yielded two isomers characterized by the relative stacking mode, staggered or eclipsed of the polyene frameworks. The isomers were termed rac and meso, respectively (Scheme 4).[4] They are obtained in thermal equilibrium, and their ratios are influenced by crystallization conditions and, principally, by the size of the R substituent. With R = H, the equilibrium is in favor of the meso form, with a 93:7 ratio.[4] Calculations carried out on the model complex $[Pd_3(C_{12}H_{14})_2]^{2+}$ assumed isolated are in keeping with the observed trend, showing the meso form to be more stable by 0.9 kcal mol^{-1}. No significant difference was either computed or observed[4] in the bond lengths of both isomers.

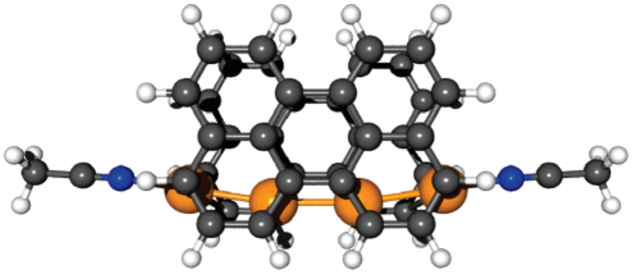


Figure 6. Representation of the equilibrium structure optimized for $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$.

5. PAHs as Ligands

5.1. $[Pd_4\text{-}(NCCH_3)_2(perylene)_2]^{2+}$. $[Pd_4\text{-}(NCCH_3)_2(C_{20}H_{12})_2]^{2+}$ was reported by Murahashi et al. as the first perylene sandwich complex having a tetranuclear metal−metal chain (Figure 6).[5]

The authors notice that the π-type frontier orbitals of perylene are antisymmetric with respect to the molecular pseudo-mirror plane containing four C atoms. These frontier MOs are delocalized on the two groups of eight carbon atoms lying on each side of this mirror plane and present phase similarities with the frontier orbitals of two octatetraene molecules.[22] This explains why the chain of metal atoms is shifted toward one edge of the eclipsed perylene dimer and clearly makes a link with a bis-tetraene−tetrapalladium chain complex previously characterized by the same group.[1] DFT calculations confirm that the $[Pd_4]^{2+}$ chain takes advantage of the *cis*,*cis*-octatetraene-like structure of the edge carbons of perylene to develop an interaction similar to the one schematized in Figure 1 and corresponding to $\eta = (2, 2, 2, 2)$. Note, however, that the coordination of the tetrapalladium chain breaks the symmetry between the two edges of the perylene molecules, which results in an important delocalization of the positive charge among the four carbon atoms contained in the pseudo-mirror plane. The computed geometrical parameters are in good agreement with the observed geometry (see Table S1 in the Supporting Information). The stabilization energy associated with one perylene molecule (ΔE) calculated for the complex without axial ligands is computed to be 6.19 eV in the gas phase, compared with 6.80 eV in the model complex formed between $[Pd_4]^{2+}$ and two *cis*,*cis*-octatetraene molecules, in spite of a better charge delocalization in perylene (Table 2).

Solvation reduces ΔE to 3.75 eV (Table 2). Finally, coordination of axial acetonitriles involves an energy of 1.12 eV only for each Pd−N bond in the isolated complex, still reduced to 0.48 eV with the COSMO model (Table 2). The extra stabilization associated with the Pd−N bond energy, computed as

$$E_{\mathrm{Pd-N}} = -\frac{E[\mathrm{Pd}_m(\mathrm{hydrocarbon})_2(\mathrm{NCCH}_3)_2]^{2+} - E[\mathrm{Pd}_m(\mathrm{hydrocarbon})_2]^{2+} - 2E[\mathrm{NCCH}_3]}{2} \quad (2)$$

appears much weaker in $[Pd_4(C_{20}H_{12})_2(NCCH_3)_2]^{2+}$ than in the model complex $[Pd_2(butadiene)_2(NCCH_3)_2]^{2+}$ (2.13 eV in the isolated molecule). This should be assigned to a competition for the positive charge between the axial ligands and the hydrocarbons, an explanation already raised to interpret the decrease of the charge transfers between metal and polyenes induced by solvation. The presence of a large positive charge on the terminal Pd atoms indeed facilitates the formation of a strong Pd−N bond. The Mulliken charge of these atoms therefore increases from +0.27e in $[Pd_4(C_{20}H_{12})_2]^{2+}$ to +0.43e in $[Pd_4(C_{20}H_{12})_2(NCCH_3)_2]^{2+}$ *at the expense of the charge transfer to the hydrocarbons*. This competition is much less intense in the butadiene complex due to the lack of possibilities for charge delocalization either along the metal framework or along the butadiene ligands. In the *solvated* complexes, the acetonitrile molecule competes with the solvent to attach the metal chain. Quite logically, the positive charge of the outermost Pd atoms and of the whole metal framework computed with COSMO remains large either with or without axial ligands, and the extra stabilization energy due to the Pd−N bond becomes weak (0.48 eV, Table 2).

5.2. Possible Stabilization of a Palladium Macrocycle with Bisanthrene and Bridging Diazo Ligands. The ability of PAHs to stabilize complex architectures of palladium atoms in sandwichlike complexes, established first with the perylene complex,[5] was recently confirmed with the characterization of a planar, cyclic cluster of five Pd atoms sandwiched between two tetracene molecules.[9] This probably means that chemical engineering, guided by a good knowledge of the bonding in these compounds, should be able to design and synthesize a large manifold of organometallic architectures belonging to that family. In that spirit, we started from the model of the $[Pd_4(C_{20}H_{12})_2(NCCH_3)_2]^{2+}$ complex to list some prerequisites for sandwiching a macrocycle mainly composed of palladium atoms:

(i) Select a specific PAH exhibiting opposite C_8 edges with *cis*,*cis*-octatetraene structures. Each of these edges should be able to stabilize a bent $(Pd_4)^{2+}$ chain. Note that perylene itself displays such a structure. However, perylene binds only one $(Pd_4)^{2+}$ chain.

(ii) In fact, two $(Pd_4)^{2+}$ strings very close to each other as they could be in perylene would develop strong repulsive electrostatic interactions, especially at both ends of the metal chains. Moreover, four carbon atoms only would be left in each PAH ligand to delocalize the positive charge transferred by two dications. Incidentally, in $[Pd_5(C_{22}H_{12})_2]^{2+}$, half of the tetracene molecules only is involved in bonding with the metal framework, the rest remaining accessible to charge delocalization. A PAH larger than perylene is therefore requested, in order to soften electrostatic repulsion and to facilitate charge delocalization. Bisanthrene $C_{28}H_{14}$ fulfills these requisites (Scheme 5).

(iii) The example of $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$ shows that stability is improved by axial coordination, although perhaps marginally (Table 2). In the case of a hypothetic $[Pd_8(bisanthrene)_2]^{4+}$, extending the two metal chains with

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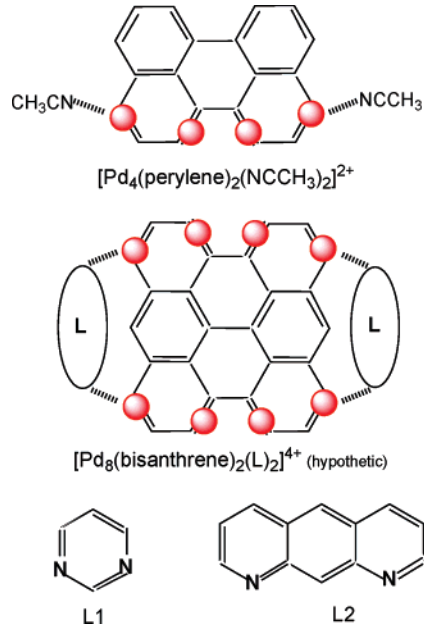
[22] Other hydrocarbon π orbitals, lower in energy and symmetric with respect to the mirror plane, also take part in the donation and allow a better delocalization of the positive charge, including on the carbon atoms embedded in the mirror plane.

Table 2. Computational Results Obtained for Some Sandwich Complexes of the Type $[Pd_{2m}(PAH)_2]^{m+}$ (PAH = Polycyclic Aromatic Hydrocarbon; m = 2, 4): Stabilization Energy Associated with One Hydrocarbon and One $(Pd_4)^{2+}$ Unit in $[Pd_{2m}(PAH)_2]^{m+}$ (ΔE_{Pd-PAH}, eV); Extra Stabilization Due to the Coordination of One Nitrogen End (ΔE_{Pd-N}, eV); Mulliken Charge of the Metal Framework [$q(Pd_{2m})$, Electrons], Metal−Metal and Metal−Nitrogen Distances (Å)[a]

complex[b]	ΔE_{Pd-PAH}		ΔE_{Pd-N}		$q(Pd_{2m})$		Pd−Pd[c]		Pd-Pd[d]	
$[Pd_4(cis,cis\text{-}C_8H_{10})_2]^{2+}$	6.80	*4.80*			0.91	*1.52*	2.60	*2.60*	2.59	*2.58*
$[Pd_4(perylene)_2]^{2+}$	6.19	*3.75*			0.70	*1.19*	2.56	*2.56*	2.54	*2.53*
$[Pd_4(perylene)_2(L)_2]^{2+}$	ibid.	*ibid.*	1.12	*0.48*	1.02	*1.21*	2.60	*2.60*	2.58	*2.57*
$[Pd_8(bisanthrene)_2]^{4+}$	4.01	*3.65*			1.21	*2.25*	2.57	*2.56*	2.55	*2.55*
$[Pd_8(bisanthrene)_2(L1)_2]^{4+}$	ibid.	*ibid.*	0.90	*0.34*	1.59	*2.30*	2.63	*2.62*	2.60	*2.59*
$[Pd_8(bisanthrene)_2(L2)_2]^{4+}$	ibid.	*ibid.*	1.65	*0.60*	1.39	*1.84*	2.61	*2.60*	2.59	*2.58*

[a] In roman, results for the complex in the gas phase; in italics, results for the solvated molecule. [b] L = $NCCH_3$; L1 = $N_2C_4H_4$; L2 = $N_2C_{12}H_8$ (see Scheme 3). [c] Outermost distances. [d] Innermost distance.

Scheme 5



$NCCH_3$ ligands would lead to steric repulsion. Bidentate ligands a priori look more appropriate and would close the macrocycle by connecting the terminal elements of both $(Pd_4)^{2+}$ strings (Scheme 5). The choice of aromatic diazo ligands, either monocyclic (L1) or tricyclic (L2) was suggested first by sterical considerations about their ability to fit in the interval between the metal chains.

The hypothetic complexes $[Pd_8(bisanthrene)_2]^{4+}$ and $[Pd_8(bisanthrene)_2(L)_2]^{4+}$, with L = L1 or L2, had their geometry fully optimized by means of DFT and their stability computed with respect to fragments, either isolated or solvated, as for the model complexes discussed above. Results are reported in Table 2, in which ΔE refers to the stabilization energy for one hydrocarbon (or one nitrogen end when axial coordination is considered) and one $(Pd_4)^{2+}$ unit, that is, 25% of the stabilization for the whole molecule. The results are therefore directly comparable to those of the $[Pd_4(perylene)_2]^{2+}$ and $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$ compounds. Results in the gas phase show that $\Delta E_{Pdm-PAH}$ has decreased from 6.19 eV for Pd_4−perylene to 4.01 eV for Pd_8−bisanthrene due to the electrostatic repulsion between the $(Pd_4)^{2+}$ units. However, the charge delocalization over the hydrocarbons is extremely efficient, since the formal 4+ charge of the metal framework has been reduced to +1.21. As expected, solvation counterbalances the charge repulsion and the ΔE value calculated with COSMO becomes similar to that computed for $[Pd_4(perylene)_2]^{2+}$ (3.65 vs 3.75 eV, Table 2). The heterocyclic axial ligands proposed for achieving the metallocyclic structure indeed contribute to the global stabilization (Table 2). The efficiency of the tricyclic ligand L2 (Scheme 5) even appears higher than that of acetonitrile in $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$ due to a good fitting to the structure of the complex and especially to an excellent ability to attract the residual charge of the metal framework through π back-donation and delocalize it over the π system of the tricyclic ligand (Figure 7). The global charge on the metal framework therefore decreases from +2.25e in solvated $[Pd_8(bisanthrene)_2]^{4+}$ to +1.84e in solvated $[Pd_8(bisanthrene)_2(L)_2]^{4+}$ (Table 2). The global stabilization for the latter complex, computed with COSMO, therefore reaches 16.99 eV, compared to 8.46 eV for $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$. On the grounds of thermodynamics, the synthesis of $[Pd_8(bisanthrene)_2(L)_2]^{4+}$ (Figure 7) therefore seems feasible.

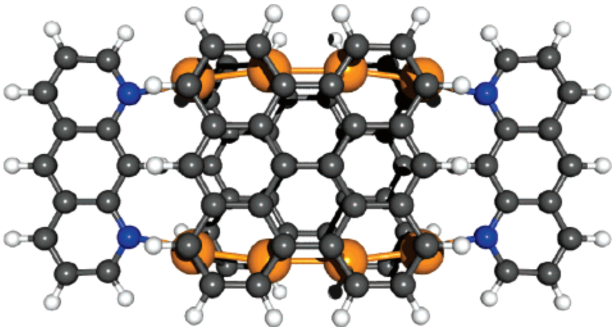


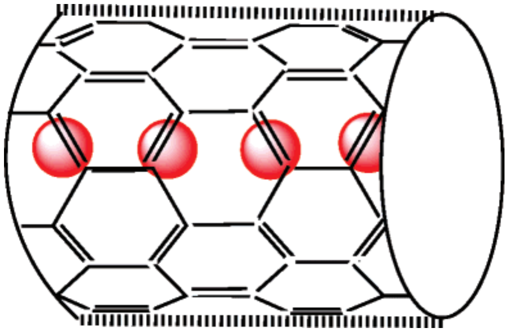
Figure 7. Representation of the equilibrium structure optimized for the hypothetic complex $[Pd_4(bisanthrene)_2(C_{12}H_8N_2)_2]^{2+}$.

6. Summary and Conclusion

The linear dicationic clusters of palladium atoms sandwiched between conjugated hydrocarbons, either polyenic or polybenzenic, exhibit a bonding pattern really distinct from those characterized for other well-documented families of metal-string complexes. The driving force to the assembly of these organometallic complexes is a strong donation from the π system of the hydrocarbons to the appropriate MO delocalized over the metal framework. The nature of this MO, unoccupied in relation with the dicationic character of the complex, depends upon the haptotropic conformations of the metal atoms. These conformations also govern the metal−metal distances, large between tri-hapto metals, short between di-hapto ones. By contrast, the role of direct metal−metal interactions appears negligible as far as the energy balance is concerned. These interactions, either weakly bonding or weakly antibonding, could contribute to delocalize the positive charge. However, this delocalization is largely conveyed via the hydrocarbon π systems. Delocalization of the positive charge transferred to the conjugated hydrocarbons extends beyond the region of bonding with palladium, whenever it is possible, and then contributes to further stabilize the complex. Solvation, crystal forces, and coordination of the palladium strings in an axial position hamper the hydrocarbon-to-metal donation since they all require a large positive charge along the metal string and, more specifically, at both ends. Therefore, the net contribution of axial coordination to the energy balance of the complex may be rather weak, especially when solvation is taken into account.

This remarkable affinity between one-, and possibly two-dimensional cationic palladium clusters on the one hand, conjugated polyenes and PAH on the other hand, opens the way to the design and synthesis of a large manifold of new compounds, extending the concept and the potentialities of sandwich complexes. On the basis of the specific pattern of this bonding interaction, some directions are proposed leading to the design of a hypothetic molecular architecture, the energetic balance of which appears equivalent to that of presently existing complexes. It also appears that carbon nanotubes could supply an environment quite favorable to the encapsulation and strong fixation of strings of metal atoms with appropriate electronic configuration[23] provided that (i) the diameter of the tube is compatible with sandwich coordination ($d \approx 4$ Å) and (ii) the arrangement of the carbon atoms on opposite sides of the tube is phased so as to reproduce the eclipsed or staggered (rac or meso) polyenic conformations observed in the sandwich complexes characterized by Kurosawa and Murahashi (Scheme 6). DFT calculations involving such models are presently in progress.

Scheme 6



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Supporting Information Available: Total energies, symmetry constraints, optimized Cartesian coordinates, Mulliken charges obtained from DFT/BP86 calculations carried out on the ground states of $[Pd_m(C_{2n}H_{2n+2})_2]^{2+}$ ($m = 2-4$, $n = 2-8$, $n \geq m$), $[Pd_4(perylene)_2]^{2+}$, $[Pd_4(perylene)_2(NCCH_3)_2]^{2+}$, $[Pd_8(bisanthrene)_2]^{4+}$, and $[Pd_8(bisanthrene)_2(L)_2]^{4+}$, and results from geometry optimizations carried out with the COSMO model. This material is available free of charge via the Internet at http://pubs.acs.org.

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