Bis(benzonitrile)palladium(II) Dihalides: Structures and Cocrystallization of the Cubic Cluster Pd_6Cl_{12} with (*E*)-Stilbene and with Bis(benzonitrile)palladium(II) Dichloride

Marilyn M. Olmstead,* Pin-pin Wei, Arwa S. Ginwalla, and Alan L. Balch*

Department of Chemistry, University of California, Davis, California 95616

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Crystals of the planar, trans complexes, bis(benzonitrile)palladium(II) dichloride and bis(benzonitrile)palladium(II) dibromide, suitable for single-crystal X-ray diffraction studies are obtained by growth from solutions in benzonitrile and their structures determined. While bis(benzonitrile)palladium(II) dichloride readily loses benzonitrile to form the cubic cluster Pd_6Cl_{12}, which cocrystallizes with a variety of planar aromatic hydrocarbon molecules, the much less soluble complex bis(benzonitrile)palladium(II) dibromide does not act as a source of the so far unknown cluster Pd_6Br_{12}. Attempts to prepare the hypothetical bis(benzonitrile)palladium(II) diiodide by reaction of PdI_2 with benzonitrile were not successful. A solution of bis(benzonitrile)palladium(II) dichloride in *p*-xylene on standing produces crystals of $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene, which contain columns of alternating Pd_6Cl_{12} and $(PhCN)_2PdCl_2$ molecules in face-to-face orientations along with similar columns in which Pd_6Cl_{12} and *p*-xylene molecules are interleaved in face-to-face arrays. A solution of bis(benzonitrile)palladium(II) dichloride and (*E*)-stilbene in benzene solution leads, not to coordination of palladium to the olefin, but to deposition of crystals of the ternary molecular compound, $Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot$2(benzene). In this solid, two Pd_6Cl_{12} clusters make face-to-face contact with phenyl rings on opposite sides of the (*E*)-stilbene molecule, but the olefinic portion is far from the palladium cluster. Additionally, one of the two benzene rings abuts the Pd_6Cl_{12} cluster in a face-to-face fashion.

Introduction

Recently, this laboratory reported that a number of supramolecular aggregates of the cubic cluster Pd_6Cl_{12} with methylated benzenes (i.e., durene and mesitylene), the fullerene C_{60}, and polynuclear aromatic hydrocarbons (i.e., naphthalene and 1,2:5,6-dibenzanthracene) can be isolated in crystalline form.[1,2] Compounds of this type, which include $Pd_6Cl_{12}\cdot$(durene), $Pd_6Cl_{12}\cdot1.5$(naphthalene), $Pd_6Cl_{12}\cdot0.5C_{60}\cdot1.5$(benzene), and $Pd_6Cl_{12}\cdot0.5$(1,2:5,6-dibenzanthracene)$\cdot0.5$(benzene), consist of individual molecules of Pd_6Cl_{12} and the flat aromatic molecules arranged in close, face-to-face proximity. These molecules are formed by simply mixing the appropriate hydrocarbon or fullerene (as a solution in benzene if it is not a liquid) with the labile complex, bis(benzonitrile)palladium(II) dichloride, and allowing the mixture to stand over a prolonged period. Eventually, deep red, air-stable crystals of the aggregates crystallize from solution. The Pd_6Cl_{12} cluster itself is soluble in aromatic solvents. Spectroscopic studies on solutions of Pd_6Cl_{12} in various methylated benzenes (i.e., mesitylene, xylene, and toluene) are consistent with charge-transfer interactions between the aromatic donors and the palladium cluster.

Here we report studies designed to form the unknown clusters Pd_6Br_{12} and Pd_6I_{12} from the corresponding bis(benzonitrile)-palladium(II) dihalides. Additionally, two new compounds that contain the Pd_6Cl_{12} cluster cocrystallized with its precursor, bis(benzonitrile)palladium(II) dichloride, and with a potential ligand, (*E*)-stilbene, are described.

In the context of this work, it should be noted that palladium(II) dichloride forms several polymorphs. The α-form consists of infinite linear chains in which each palladium atom is coordinated by four chlorine atoms in a square, while each chlorine atom bridges two palladium atoms.[3] The *β*-form consists of discrete molecules of Pd_6Cl_{12}.[4−6] This cluster has an octahedral array of palladium atoms that are surrounded by four equivalent chlorine atoms.[6] Each chlorine atom bridges an edge of the cube that can be inscribed about the octahedron of palladium atoms. The cluster-containing *β*-form of palladium(II) dichloride can be prepared in several ways. Treatment of Pd_3(acetate)$_6$ with carbon monoxide in glacial acetic acid with some perchloric acid yields polycrystalline Pd_6Cl_{12}.[5] Larger, single, crystals of Pd_6Cl_{12} may be prepared by gradual precipitation of Pd_6Cl_{12} from a benzene/chloroform solution of bis(benzonitrile)palladium(II) dichloride or by the slow decarbonylation of $Pd_2(\mu\text{-}Cl)_2Cl_2(CO)_2$ in thionyl chloride.[6] Commercial $PdCl_2$ is not soluble in aromatic solvents and has been reported to consist of another polymorph of currently unknown structure.[7] The solid-state structure of palladium(II) dibromide has been shown to consist of infinite linear chains, $\cdots PdBr_2PdBr_2\cdots$, that are similar to the chains seen in α-$PdCl_2$.[8] Several polymorphs of PdI_2 are known; the *β*-phase has a complex structure consisting of planar Pd_2I_6 units.[9] However, solid phases containing the discrete clusters Pd_6Br_{12} and Pd_6I_{12} are, to our

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10.1021/ic0000597 CCC: \$19.00

Table 1. Selected Interatomic Distances and Angles for $(PhCN)_2PdX_2$ Complexes

	$(PhCN)_2PdCl_2$	$(PhCN)_2PdBr_2$		$Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot p$-xylene
		molecule 1	molecule 2	
		Bond Lengths (Å)		
Pd–N	1.974(2)	1.99(2) 1.94(2)	1.955(14)	1.976(6)
Pd–X	2.2857(8)	2.427(2)	2.407(2)	2.296(2)
N–C	1.141(3)	1.16(3) 1.12(3)	1.13(2)	1.137(8)
		Bond Angles (deg)		
N–Pd–N	180	180	180	180
X–Pd–X	180	179.5(1)	180	180
N–Pd–X	90.52(7) 89.48(7)	89.8(1) 90.2(1)	90.3(4) 89.7(4)	90.4(2) 89.6(2)
C–N–Pd	177.9(2)	180 180	175.6(15)	172.9(6)

Table 2. Crystallographic Data

	$(PhCN)_2PdCl_2$	$(PhCN)_2PdBr_2$	$Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot p$-xylene	$Pd_6Cl_{12}\cdot0.5$(stilbene)$\cdot2$(benzene)
empirical formula	$C_{14}H_{10}Cl_2N_2Pd$	$C_{14}H_{10}Br_2N_2Pd$	$C_{22}H_{20}Cl_{14}N_2Pd_7$	$C_{19}H_{18}Cl_{12}Pd_6$
fw	383.54	472.5	1553.50	1310.13
a, Å	5.715(2)	8.272(3)	16.550(5)	11.383(2)
b, Å	8.277(2)	20.529(9)	15.489(4)	12.155(2)
c, Å	8.576(2)	18.102(7)	15.850(4)	12.803(2)
α, deg	116.05(2)	90	90	78.050(14)
β, deg	95.09(2)	97.43(2)	109.91(2)	67.70(2)
γ, deg	93.31(2)	90	90	80.16(2)
V, Å^3	360.9(2)	3048(2)	3820(2)	1595.0(5)
Z	1	8	4	2
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
color	pale red	yellow orange	dark red	dark red
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ, g/cm^3	1.765	2.059	2.701	2.728
μ, mm^{-1}	1.641	6.447	4.221	4.329
max–min transm	0.93–0.69	0.78–0.42	0.87–0.64	0.70–0.57
R1^a (obsd data)	0.026	0.068	0.042	0.047
wR2^b (all data, F^2 refinement)	0.063	0.068^c	0.105	0.129

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_o^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

knowledge, unknown, whereas the series of clusters $Pd_6Cl_{12-n}Br_n$ where $n = 1-12$ has been detected in the gas phase from vaporization of mixtures of $PdCl_2$ and AgBr.[10] The analogous cubic platinum clusters, Pt_6Cl_{12} and Pt_6Br_{12}, have been isolated,[11,12] but their ability to cocrystallize with organic molecules has not been explored.

Results

Bis(benzonitrile)palladium(II) dichloride is a labile complex which readily loses benzonitrile to form complexes with coordinated $PdCl_2$ groups or Pd_6Cl_{12} in the absence of strongly ligating molecules.[13,14] To obtain crystals of bis(benzonitrile)palladium(II) dichloride itself, it was necessary to use benzonitrile as the solvent to prevent loss of this ligand from the complex. Crystals of bis(benzonitrile)palladium(II) dibromide were grown similarly from benzonitrile solution. However, bis(benzonitrile)palladium(II) dibromide is much less soluble than bis(benzonitrile)palladium(II) dichloride, and despite numerous attempts, we have been unable to find conditions under which the hypothetical cluster Pd_6Br_{12} can be formed from bis(benzonitrile)palladium(II) dibromide. Heating a benzene solution of bis(benzonitrile)palladium(II) dibromide at its boiling point for 14 h produced only α-$PdBr_2$ with an X-ray powder pattern identical to that obtained previously.[8] Additionally, attempts to prepare the unknown complex bis(benzonitrile)palladium(II) diiodide by treatment of solid palladium(II) iodide with hot benzonitrile did not produce the expected product; indeed, the palladium(II) iodide does not dissolve in neat, hot benzonitrile. We presume that the Pd–I bonds in solid palladium(II) iodide are simply too strong to undergo displacement by benzonitrile, which is generally a weakly bound ligand.

Upon standing, the dark red solution formed by dissolving bis(benzonitrile)palladium(II) dichloride in *p*-xylene gradually produced crystals of the ternary compound $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot p$-xylene that were suitable for X-ray diffraction. Similarly, dissolution of bis(benzonitrile)palladium(II) dichloride in benzene in the presence of (*E*)-stilbene produced deep red crystals of $Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot2$(benzene). The structures of each of these compounds were determined by single-crystal X-ray diffraction. Relevant data for these crystal structures and their determinations are summarized in Tables 1 and 2.

Structures of Bis(benzonitrile)palladium(II) Dichloride and Bis(benzonitrile)palladium(II) Dibromide. Figure 1 shows perspective drawings of *trans*-$(PhCN)_2PdCl_2$ and *trans*-$(PhCN)_2PdBr_2$. Selected bond distances and angles are given in Table 1. Figures 2 and 3 compare the solid-state packings within the two compounds.

Bis(benzonitrile)palladium(II) dichloride crystallizes with half

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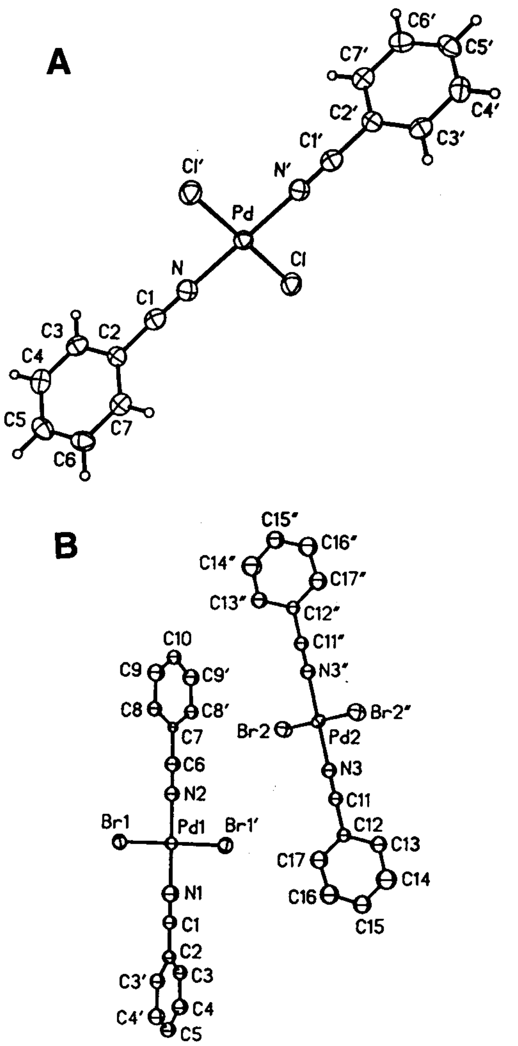

Figure 1. Molecular structures of (A) *trans*-$(PhCN)_2PdCl_2$ and (B) the two independent molecules of *trans*-$(PhCN)_2PdBr_2$.

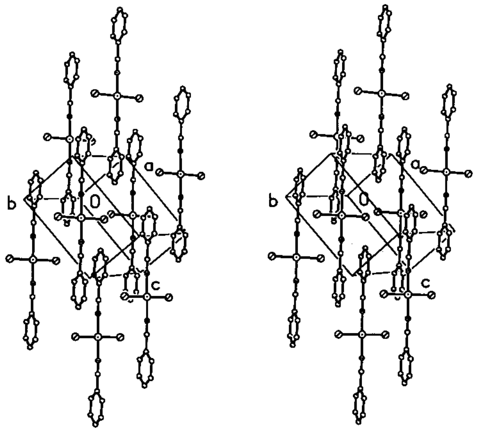

Figure 2. Stereoview of the solid-state packing in *trans*-$(PhCN)_2PdCl_2$.

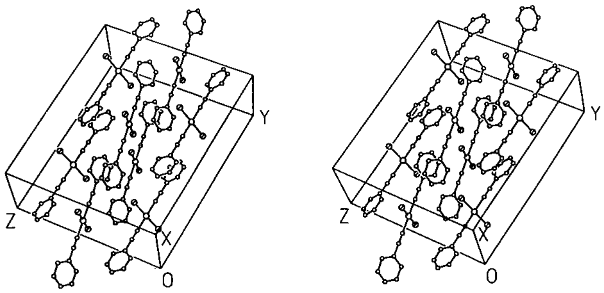

Figure 3. Stereoview of the solid-state packing in *trans*-$(PhCN)_2PdBr_2$.

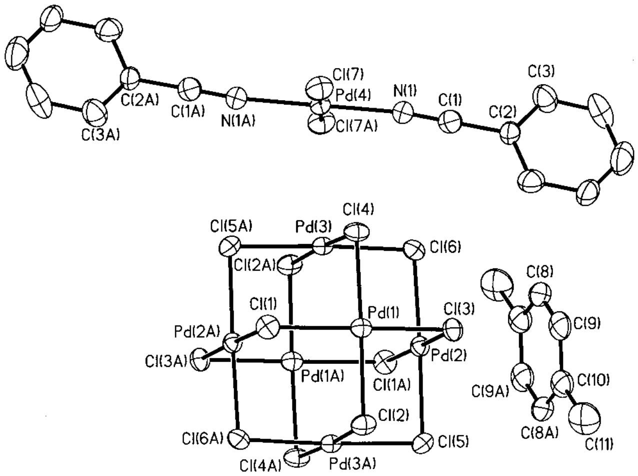

Figure 4. Molecular components present in $Pd_6Cl_{12}\cdot$*trans*-$(PhCN)_2PdCl_2\cdot$*p*-xylene.

of the molecule in the asymmetric unit and with the other half generated by inversion through a center of symmetry. The bond distances and angles in the complex fall within normal ranges. Bis(benzonitrile)palladium(II) dibromide crystallizes with two half-molecules in the asymmetric unit. For the molecule containing Pd(1), the other half of the molecule is generated by reflection through a mirror plane which passes through the palladium atoms and the coordinated nitrile moiety. For the molecule containing Pd(2), the remainder of the molecule is generated by inversion through the crystallographic center of symmetry. The coordination environments of both molecules of $(PhCN)_2PdBr_2$ are similar to each other and to that of $(PhCN)_2PdCl_2$. The two molecules of $(PhCN)_2PdBr_2$ differ owing to rotations of the planes of the phenyl rings about the NC−Ph axes.

As seen in Figures 2 and 3, the molecular packings of $(PhCN)_2PdCl_2$ and $(PhCN)_2PdBr_2$ in the solid state differ. In the structure of $(PhCN)_2PdCl_2$, the phenyl rings are in parallel planes but do not make face-to-face contact. However, there are close contacts (2.68 Å for H(7) and 2.82 Å for H(5)) between aromatic hydrogen atoms of one molecule and the chloride ligands on adjacent molecules. The molecular packing in $(PhCN)_2PdBr_2$ shows regions of face-to-face contacts between the phenyl rings of adjacent molecules as seen in Figure 3. The separation of the parallel phenyl rings is 3.37 Å, which is consistent with typical $\pi-\pi$ contact between aromatic rings.[15] There are also a close contact of an aromatic hydrogen atom with the bromide ligand of an adjacent molecule (distance to H(17) 2.94 Å) and a short Br(2)−Br(2′) separation of 3.532 Å.

$Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene. Figure 4 shows a drawing of the three different molecules that are present. There are crystallographic centers of symmetry located within each of these three molecules. No unusual geometric distortions are observed in any of the molecular structures in this solid. For example, as seen in Table 1, the $(PhCN)_2PdCl_2$ molecule in $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene has geometric parameters that are very close to those found in crystalline $(PhCN)_2PdCl_2$ itself.

The molecular packing of these components within crystalline $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene is shown in Figure 5. As seen

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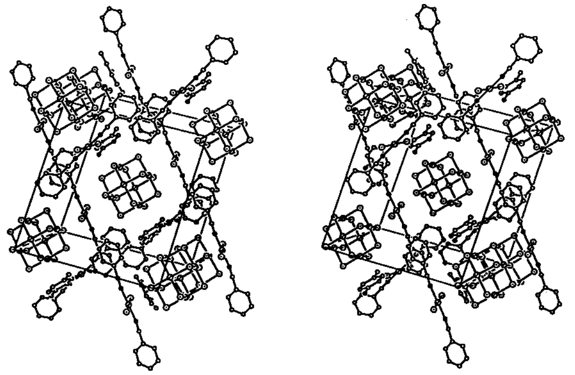

Figure 5. Stereoview of the solid-state molecular packing in $\mathrm{Pd_6Cl_{12}}$·*trans*-$\mathrm{(PhCN)_2PdCl_2}$·*p*-xylene.

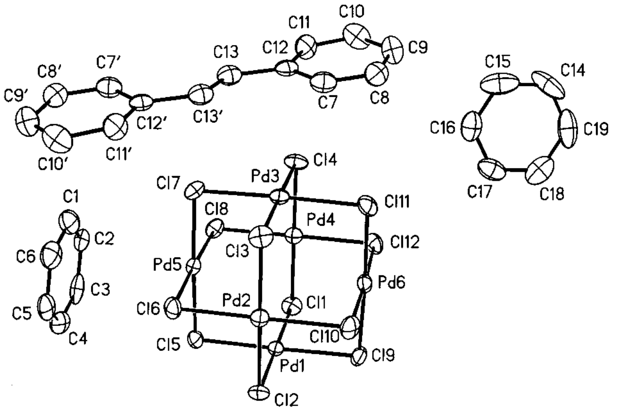

Figure 6. Molecular components present in $\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene)·2(benzene).

in other compounds where $\mathrm{Pd_6Cl_{12}}$ crystallizes with aromatic molecules, the solid consists of columns of alternating $\mathrm{Pd_6Cl_{12}}$ and *p*-xylene molecules which make parallel, face-to-face contacts. Additionally, there are columns of alternating $\mathrm{Pd_6Cl_{12}}$ and $\mathrm{(PhCN)_2PdCl_2}$ molecules in which the $\mathrm{PdCl_2N_2}$ units are parallel to $\mathrm{PdCl_4}$ faces of the cluster. In both cases, the surfaces are offset from one another. For the $\mathrm{Pd_6Cl_{12}}$/*p*-xylene interaction, the closest Pd···C contacts involve C(9), which is 3.402 Å from Pd(2), and C(8), which is 3.484 Å from Pd(2). For the $\mathrm{Pd_6Cl_{12}}$/$\mathrm{(PhCN)_2PdCl_2}$ interaction, the Pd(3)−Pd(4) distance is 3.358 Å, while the Pd(3)−Cl(7′) distance is 3.434 Å and the Pd(4)−Cl(4) distance is 3.544 Å. The phenyl rings of the $\mathrm{(PhCN)_2PdCl_2}$ portion do not make face-to-face contact with the $\mathrm{Pd_6Cl_{12}}$ clusters.

$\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene)·2(benzene). Figure 6 shows a view of the four different molecules that are present in the solid and gives some idea of their relative orientations. The (*E*)-stilbene molecule resides on a crystallographic center of symmetry, while the other three molecules do not have any crystallographically imposed symmetry. Both the (*E*)-stilbene molecule and one of the benzene molecules (benzene-1) make parallel, face-to-face contacts with the $\mathrm{Pd_6Cl_{12}}$ cluster. On the other hand, benzene-2, which shows evidence of libration about its center, does not make any such contact with the $\mathrm{Pd_6Cl_{12}}$ cluster. Figure 7 shows a stereoview of the overall organization of these units in the solid state. There are columns of alternating benzene molecules and $\mathrm{Pd_6Cl_{12}}$ clusters that run roughly along the *a* axis. The $\mathrm{Pd_6Cl_{12}}$ cluster is offset toward one corner of the benzene molecule. The shortest contacts between atoms of these units are Pd(5)···C(2) at 3.27 Å and Pd(5)···C(3) at 3.46 Å. Two $\mathrm{Pd_6Cl_{12}}$ clusters interact with each (*E*)-stilbene molecule and are located on opposite faces of the (*E*)-stilbene molecule. The distances from Pd(3) to the nearest carbon atoms are as follows: to C(12), 3.38 Å; to C(7), 3.50 Å; and to C(13), 3.46 Å. Notice that the olefinic portion is not coordinated to palladium but that the phenyl rings of the (*E*)-stilbene molecule make face-to-face contacts with the $\mathrm{Pd_6Cl_{12}}$ cluster. Additionally, $\mathrm{Pd_6Cl_{12}}$ clusters make face-to-face contacts with one another as is also seen in pristine $\mathrm{Pd_6Cl_{12}}$ itself and many of its cocrystals.

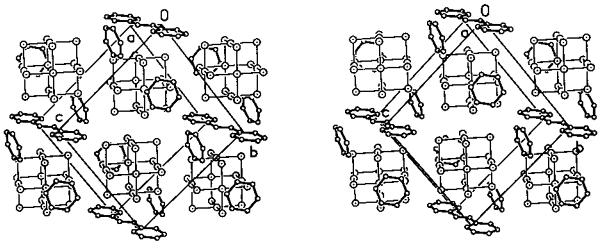

Figure 7. Stereoview of the solid-state molecular packing in $\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene)·2(benzene).

The molecular structures and internal motions of (*E*)-stilbenes in crystalline environments have been the subject of considerable interest.[16−18] In crystals of (*E*)-stilbene itself, there are two independent half-molecules (α and β) in the asymmetric unit. The α sites display orientational disorder, and the ethylene bond lengths at both sites are shorter (by 0.05 and 0.02 Å) than expected (1.337 Å) for a normal ethylene bond. In $\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene) ·2(benzene), scattering is dominated by the heavy $\mathrm{Pd_6Cl_{12}}$ cluster. Consequently, the precision of the geometric parameters for the (*E*)-stilbene molecule in this cocrystal are lower than those obtained for simple crystalline stilbenes. However, in $\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene)·2(benzene), there is no sign of disorder of the (*E*)-stilbene molecule and the olefinic link has a length (1.36(2) Å) that is somewhat long.

Discussion

The results reported here demonstrate the difficulties in extending the synthesis of the cubic cluster $\mathrm{Pd_6Cl_{12}}$ from the complex bis(benzonitrile)palladium(II) dichloride to other halides. Although bis(benzonitrile)palladium(II) dibromide has been prepared and structurally characterized, it has very limited solubility and has not been found to yield $\mathrm{Pd_6Br_{12}}$ in any form. $\mathrm{PdI_2}$ is insoluble in benzonitrile and does not form bis(benzonitrile)palladium(II) diiodide. The hypothetical cluster $\mathrm{Pd_6I_{12}}$ also remains unknown.

Solutions of bis(benzonitrile)palladium(II) dichloride continue to deposit new crystalline phases that contain the cluster $\mathrm{Pd_6Cl_{12}}$. Thus, a solution of bis(benzonitrile)palladium(II) dichloride in *p*-xylene results not only in cocrystallization of $\mathrm{Pd_6Cl_{12}}$ with molecules of the solvent but also in cocrystallization with the precursor complex, bis(benzonitrile)palladium(II) dichloride, to form the ternary material, $\mathrm{Pd_6Cl_{12}}$·$\mathrm{(PhCN)_2PdCl_2}$·*p*-xylene. Additionally, $\mathrm{Pd_6Cl_{12}}$ has been found to cocrystallize rather than coordinate with (*E*)-stilbene to form another ternary material, $\mathrm{Pd_6Cl_{12}}$·0.5((*E*)-stilbene)·2(benzene).

The following set of rules have been suggested for the analysis of structures that involve cocrystallization of $\mathrm{Pd_6Cl_{12}}$ and molecules with conjugated π-systems:[2] (1) The planar π-conjugated molecules are sandwiched between $\mathrm{Pd_6Cl_{12}}$ clusters and make face-to-face contacts with these clusters on both

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sides. (2) In cases where two different π-conjugated molecules are present within the solid, the molecule with the lower ionization potential preferentially makes face-to-face contact with the Pd_6Cl_{12} cluster. (3) Individual Pd_6Cl_{12} clusters interact with pairs of planar π-conjugated molecules in a face-to-face arrangement on two opposite faces of the cluster. (4) Pd_6Cl_{12} clusters interact with one another through nearly parallel, face-to-face contacts, with the closest contacts generally between a palladium atom of one cluster and a chlorine atom of another.

The structure of $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene conforms to the above rules without exception, whereas the structure of $Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot$2(benzene) obeys these rules with one exception. Although the benzene/Pd_6Cl_{12} arrangement in $Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot$2(benzene) conforms to rule 3 so that columns of alternating molecules of benzene and Pd_6Cl_{12} are found, the (*E*)-stilbene/Pd_6Cl_{12} interaction is different, as seen in Figure 7. While there is a face-to-face arrangement of an (*E*)-stilbene molecule on one side of the cluster, there is no (*E*)-stilbene molecule aligned parallel to the opposite face of the cluster. Rather there is a face-to-face cluster/cluster contact in its place.

Experimental Section

Preparations. Bis(benzonitrile)palladium(II) Dichloride. This compound was prepared as described in the literature.[19]

For crystal growth, 100 mg (0.261 mmol) of bis(benzonitrile)palladium(II) dichloride was dissolved in 2 mL of benzonitrile. The resulting dark orange solution was transferred to a 10 mL beaker and heated for 60 min at 100 °C. Dark red crystals formed as the solution partially evaporated and then cooled. The crystals were collected by filtration and washed with diethyl ether. Yield: 21.5 mg (0.0561 mmol, 21.5%).

Bis(benzonitrile)palladium(II) Dibromide. Palladium(II) dibromide (0.5386 g, 2.02 mmol) was added to 15 mL (147 mmol) of benzonitrile. The mixture was heated to 140 °C for 1 h. The resulting dark red solution was quickly filtered while hot to remove any unreacted palladium(II) dibromide. A 70 mL portion of diethyl ether was added, and the solution was chilled to 0 °C for 5 min. The powdery orange solid that formed was collected by filtration on a glass frit and washed with diethyl ether. Yield: 0.594 g (1.26 mmol, 62.4%).

For crystal growth, 100 mg (0.211 mmol) of bis(benzonitrile)palladium(II) dibromide was dissolved in 2 mL of benzonitrile. The resulting dark red solution was transferred to a 10 mL beaker and heated for 60 min at 100 °C. Dark red crystals formed as the solution evaporated and then cooled. The crystals were collected by filtration and washed with diethyl ether. Yield: 15 mg (0.032 mmol, 15%).

$Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene. A 150 mg (0.391 mmol) sample of bis(benzonitrile)palladium(II) dichloride was dissolved in 10 mL (81.6 mmol) of *p*-xylene. The resulting dark red solution was shaken and filtered. The filtrate was placed in 5 mm od glass tubes, which were then set aside for 1 week. The crystals were harvested by cracking the tubes and collecting the solid by filtration, followed by rapid washings with *p*-xylene and then ether. Yield: 25.7 mg (0.0165 mmol, 25.4%).

$Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot$2(benzene). Samples of 314.4 mg (1.744 mmol) of (*E*)-stilbene and 96.4 mg (0.251 mmol) of bis(benzonitrile)palladium(II) dichloride were dissolved in 3 mL of benzene. The resulting dark red solution was filtered, and the filtrate was placed in 5 mm od glass tubes, which were then set aside for 3 weeks. The crystals were harvested by cracking the tubes and collecting the solid by filtration, followed by a rapid washing with benzene. Yield: 43.4 mg (0.033 mmol, 79.2%).

X-ray Crystallography. The crystals together with small amounts of the mother liquor were removed from the glass tube in which they had been prepared and immediately coated with a hydrocarbon oil on a microscope slide.[20] Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold stream of a Siemens R3m/V diffractometer equipped with an Enraf-Nonius low-temperature apparatus. The diffractometer utilized a sealed Mo tube that operated at 2 kW and a graphite monochromator. All the data sets were collected at 130(2) K. Only random fluctuations of less than 2% were observed in the check reflections for all data sets. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[21] The structures were solved by Patterson or direct methods using the software of SHELXTL 5 and were refined on the basis of F^2, except in the case of bis(benzonitrile)palladium(II) dibromide, where SHELXTL PLUS, VMS version, was used and the structure was refined with the program SHELXTL-93 (based on F). Absorption corrections were applied to the structures with the program XABS2, which calculates 24 coefficients from a least-squares fit of $1/A$ vs $\sin^2(\theta)$ to a cubic equation in $\sin^2(\theta)$ by minimization of F_o^2 and F_c^2 differences.[22] Hydrogen atoms were added geometrically and refined with a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters, except in the case of bis(benzonitrile)palladium(II) dibromide, where only palladium and bromine atoms were treated anisotropically.

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Supporting Information Available: Listings of X-ray experimental details, atomic coordinates, thermal parameters, bond lengths, and bond angles for bis(benzonitrile)palladium(II) dichloride, bis(benzonitrile)palladium(II) dibromide, $Pd_6Cl_{12}\cdot(PhCN)_2PdCl_2\cdot$*p*-xylene, and $Pd_6Cl_{12}\cdot0.5$((*E*)-stilbene)$\cdot$2(benzene). This material is available free of charge via the Internet at http://pubs.acs.org.

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