

Preparation and Structure of Two Binuclear Sandwich Benzene–Metal Complexes of Palladium

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Abstract: The reaction of AlCl_3 , Al, and PdCl_2 in boiling benzene produces two diamagnetic crystalline complexes of formulas $[\text{PdAl}_2\text{Cl}_7\text{C}_6\text{H}_6]_2$ (A) and $[\text{PdAlCl}_4\text{C}_6\text{H}_6]_2$ (B). Their structures were determined by single-crystal X-ray diffraction methods. Both molecules are centrosymmetric with the center of symmetry at the midpoint between the two bonded Pd atoms. The two benzene rings are π -bonded to both Pd atoms giving rise to a binuclear sandwich structure. In complex A a partial statistical disorder is present, and the structure is interpreted on the basis of two equally probable arrangements of the benzene rings. In complex B the symmetry of the molecular core corresponds to the D_{2h} group, and each benzene ring may be formally assumed to act as a conjugated diene, π -coordinating two Pd atoms. Principal crystallographic data are the following. Complex A: $a = 9.42 \pm 0.03$ Å; $b = 9.24 \pm 0.03$ Å; $c = 9.56 \pm 0.03$ Å; $\alpha = 77.9 \pm 0.5^\circ$; $\beta = 96.2 \pm 0.5^\circ$; $\gamma = 108.1 \pm 0.3^\circ$; space group $P\bar{1}$; final R factor is 0.078 for 2218 reflections collected by Weissenberg method. Complex B: $a = 14.04 \pm 0.04$ Å; $b = 11.02 \pm 0.03$ Å; $c = 17.72 \pm 0.05$ Å; $\beta = 52.4 \pm 0.3^\circ$; space group $C2/c$; final R factor is 0.092 for 1397 reflections.

Fischer and coworkers have prepared several bis-arene complexes of transition metals, e.g., V,¹ Cr,² Mo,³ Re,⁴ Fe,⁵ Co,⁶ and Ni,⁷ by reaction of a transition metal chloride with AlCl_3 and Al in the presence of an aromatic hydrocarbon. All these complexes are characterized by a sandwich structure, where one metal atom is coordinated to two arene groups. The reaction of AlCl_3 , Al, and PdCl_2 in benzene produces two bis-arene complexes of an entirely new type, however. These compounds have the formulas $[\text{PdAl}_2\text{Cl}_7\text{C}_6\text{H}_6]_2$ (A) and $[\text{PdAlCl}_4\text{C}_6\text{H}_6]_2$ (B), where two directly bonded Pd atoms are sandwich-coordinated to two arene groups.

A preliminary short communication on the preparation and structure of A⁸ has already been published. In this paper we give a detailed description of the preparation of both complexes, as well as of their structures, as determined by three-dimensional X-ray analyses.

Experimental Section

Reactants. Benzene (>99% pure) was dehydrated by refluxing over sodium, then distilled, and stored over molecular sieves under nitrogen. PdCl_2 was used as the anhydrous salt, with a purity >99%. AlCl_3 was sublimed just before use.

Preparation of the Two Complexes. Anhydrous benzene (50 cc), PdCl_2 (1 g, 5.64 mmoles), AlCl_3 (1.2 g, 9 mmoles), and Al powder (0.5 g) were introduced into a 200-cc glass flask supplied with a magnetic stirrer, under an anhydrous N_2 atmosphere. The mixture was stirred under reflux for about 30 min, then filtered hot (G-3 sintered glass filter) into a 200-cc cylindrical container, which was immersed in a thermostated bath at 80° . The filter had been previously heated with a free flame, in order to prevent precipitation of oils during filtration. The clear dark brown solution was then

allowed to cool very slowly (2–3 days) to room temperature. After this time, well-grown crystals with a deep brown color were found on the walls of the container. The mother liquor was removed with a syringe, and the crystals were washed with about 20 cc of anhydrous degassed benzene, then with pentane, and finally dried under vacuum at room temperature. The analysis of big well-shaped crystals, isolated mechanically from the microcrystalline powder that is sometimes present, is as follows. *Anal.* Calcd for $[\text{PdAl}_2\text{Cl}_7\text{C}_6\text{H}_6]_2$ (A): C, 14.85; H, 1.2; Cl, 51.4; Pd, 21.3; Al, 11.3. Found: C, 14.78; H, 1.1; Cl, 51.2; Pd, 20.9; Al, 11.0.

When using an amount of AlCl_3 higher than that indicated above ($\text{AlCl}_3/\text{PdCl}_2$ molar ratio from ~ 1.6 to ~ 2) an oil was deposited, which crystallized only in part.

Following the above procedure, but employing 0.75 g (5.64 mmoles) of AlCl_3 instead of 1.2 g, well-formed, deep brown crystals were obtained. *Anal.* Calcd for $[\text{PdAlCl}_4\text{C}_6\text{H}_6]_2$ (B): C, 20.55; H, 1.7; Cl, 40.6; Al, 7.7; Pd, 29.4. Found: C, 20.10; H, 1.7; Cl, 40.1; Al, 7.4; Pd, 28.9.

The crystals of both A and B are insoluble in benzene or *n*-hexane even at boiling temperature. Since the crystals were deposited from a hot benzene solution, the structures of the complexes in solution before crystallization may be different from those found in the crystals.

When crystals of A or B are treated with THF (freshly distilled over LiAlH_4) or ethanol, they deposit metallic Pd and PdCl_2 in equivalent amounts. This indicates that A and B can formally be considered as complexes of Pd(I). Gas chromatography of the THF or ethanol solutions shows the presence of benzene in a 1:1 molar ratio, with respect to Pd, for either complex.

Measurements of magnetic susceptibilities (Gouy balance) indicate that both A and B are diamagnetic.

The infrared spectra (Nujol mulls; Perkin–Elmer Model 225 instrument equipped with grating) exhibit the following bands. Complex A: 3060 m, 1600 s, 1580 vs, 1490 s, 1400 s, 1185 w, 1160 m, 1150 m, 1030 m, 978 w, 946 m, 780 s, 752 vs, 690 vs, 672 vs, 570 vs, 542 s, 450 s, 380 w, 356 m, 331 m, 225 m. Complex B: 3070 m, 1582 m, 1567 m, 1491 m, 1400 m, 1360 s, 1339 m, 1160 m, 1016 m, 990 m, 978 m, 950 m, 800 w, 755 s, 671 s, 592 m, 520 vs, 430 vs, 339 s, 228 s.

X-Ray Analysis of Single Crystals. For both complexes, single crystals of spherical shape, approximately 0.3 mm in diameter, were selected. Since they decompose rather rapidly in the air, they were introduced into thin glass tubes, filled with vaseline. In either case, Weissenberg equiinclination multiple-film spectra were taken along two axes. The intensity data were then reduced to a single scale factor. Mo $K\alpha$ radiation was utilized in each case and no correction for X-ray absorption was applied ($\mu R < 0.2$). The reflections could be observed until about $d = 0.7$ Å.

In the case of complex A, the crystals were rotated about the

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- (6) E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, **1**, 307 (1964).
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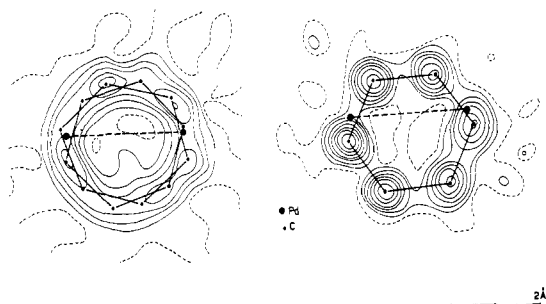


Figure 1. Sections of the electron densities through the average plane of the benzene ring for A (left) and B (right). Contours are drawn at 1 (dotted line), 2, 3, etc., $e/\text{Å}^3$. The centers of the C and of the Pd (projected) atoms are also indicated.

c axis ($l = 0-5$) and the b axis ($k = 0-4$); in addition, the $0kl$ layer was also measured.

In the case of complex B, the crystals were rotated about the b axis ($k = 0-11$) and about the $[110]$ zone axis (three levels). The scaling of the intensity data was obtained by evaluation of the scale factors of all different layers by applying a least-squares technique.

Computing Details. Atomic scattering factors were evaluated with the formula⁹

$$f_i = A_i \exp(-a_i x^2) + B_i \exp(-b_i x^2) + C_i$$

$$x = \sin^2 \vartheta / \lambda^2$$

where the atomic parameters are those given by Moore.¹⁰ Four distinct FORTRAN IV programs were used for the intensity scaling,¹¹ structure factor calculation,¹² three-dimensional Fourier synthesis,¹³ and least-squares processing.¹⁴ All computations were carried out at the Computing Center of the Polytechnic Institute of Milan (7040 IBM).

Structural Results

Complex A. Table I reports the parameters of the triclinic unit cell. The experimental density is in agreement with that calculated on the basis of one dimeric molecule in the unit cell. The space group was assumed to be $P\bar{1}$ with the dimeric molecule at the center of symmetry.

Table I. Cell Parameters of A and B

	A	B
a , Å	9.42 ± 0.03	14.04 ± 0.04
b , Å	9.24 ± 0.03	11.02 ± 0.03
c , Å	9.56 ± 0.03	17.72 ± 0.05
α , deg	77.9 ± 0.5	
β , deg	96.2 ± 0.5	52.4 ± 0.3
γ , deg	108.1 ± 0.3	
Z	1	4
Space group	$P\bar{1}$	$C2/c$
D_{calcd} , g/cm ³	2.08	2.16
D_{exptl} , g/cm ³	1.86	1.98

From the $(hk0)$, $(h0l)$, and $(0kl)$ reflections we obtained, with the use of two-dimensional Patterson and Fourier syntheses, first approximation coordinates for all atoms. This provided us with all fundamental features of the structure ($R = \Sigma \Delta F / \Sigma F_o = 0.152$ for 900 observed reflections).⁸ We then refined the atomic

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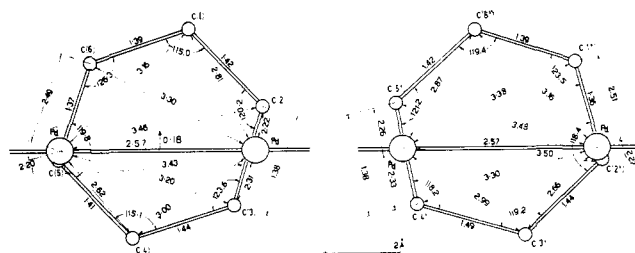


Figure 2. Arene-to-metal coordination in complex A in a view perpendicular to the benzene plane. The two distinct orientations of the ring resulting from the least-squares refinement are shown. The significant interatomic distances (Å) and bond angles (deg) are shown; for the corresponding esd's, see Table III.

parameters by the least-squares method using the 2213 independent nonzero reflections observed; a total of 3151 reflections were investigated. The observed convergence of the least-squares cycles was satisfactory for all atoms except the carbon atoms; their thermal parameters were abnormally anisotropic and the resulting geometry of the benzene group was unacceptable.

A section of the three-dimensional Fourier map through the mean plane of the benzene ring revealed a distribution of the electronic density that is almost uniformly spread along the ring (Figure 1). This distribution indicated an overlap of two coplanar, concentric benzene rings, with different angular orientations around their centers. After block-diagonal refinement of all heavy atoms in the structure, we applied five full-matrix, least-squares cycles to the benzene group only, assuming that the two different orientations are equally probable. A satisfactory convergence was obtained; final values of the same order of magnitude were found for the thermal parameters of all the carbon atoms, assumed as isotropic (Table II). If the fairly high standard deviations of the bond lengths and angles are taken into account (Table III), the geometry of the two resulting benzenes is satisfactory (Figure 2).

The final disagreement index is $R = 0.078$ for the 2213 observed reflections, and $R = 0.14$ when the 944 undetectable reflections are included.¹⁵ Figure 3 shows the stereochemistry of the heavy atoms.

Complex B. Table I reports the parameters of the monoclinic unit cell. The experimental density is in agreement with the value calculated assuming four dimeric molecules in the unit cell. Systematic absences indicate space groups Cc and $C2/c$ are possible. Patterson projections along b and along $(a + b)$ were well explained on the basis of a centrosymmetric array of eight Pd atoms.

By applying Fourier methods to the above projections, we were able to locate all atoms heavier than carbon; the space group assumed was $C2/c$. In the space group, the molecule contains a crystallographic symmetry center, as was the case of complex A. Carbon atoms were located from a three-dimensional Fourier map. Unlike the structure of the previous complex, the benzene ring is in this case unaffected by any par-

(15) The full list of observed and calculated structure factors has been deposited as Document No. NAPS 00727 with ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

Table II. Fractional Coordinate and Thermal Parameters (\AA^2) with Their Standard Deviations

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Complex A									
Pd	0.0575 (1)	0.0759 (1)	0.1007 (1)	2.32 (3)	3.54 (3)	3.73 (4)	0.38 (3)	0.38 (3)	-1.37 (3)
Cl(1)	0.1657 (4)	0.2022 (4)	0.3053 (4)	4.81 (15)	2.63 (12)	3.77 (14)	0.85 (11)	-0.43 (11)	-0.94 (11)
Cl(2)	0.2759 (4)	0.4886 (3)	0.4830 (4)	6.11 (18)	2.41 (11)	3.26 (13)	1.14 (12)	-0.45 (12)	-0.61 (10)
Cl(3)	-0.0003 (4)	0.5041 (5)	0.2030 (4)	4.10 (16)	6.70 (22)	6.14 (21)	2.77 (15)	-0.98 (14)	-1.11 (17)
Cl(4)	0.3675 (4)	0.5623 (4)	0.1185 (4)	5.65 (19)	4.62 (17)	4.64 (18)	1.03 (14)	2.06 (14)	0.15 (14)
Cl(5)	0.1519 (4)	0.8131 (4)	0.4522 (4)	4.73 (16)	4.48 (16)	5.85 (20)	2.51 (13)	-1.22 (14)	-0.58 (15)
Cl(6)	0.3999 (4)	0.7105 (4)	0.7334 (3)	4.56 (15)	5.14 (17)	3.59 (15)	1.57 (13)	-1.07 (12)	-1.31 (13)
Cl(7)	0.5184 (4)	0.8537 (5)	0.3765 (4)	5.47 (19)	5.00 (19)	6.28 (22)	-0.25 (15)	-2.80 (16)	-1.02 (17)
Al(1)	0.1982 (4)	0.4489 (4)	0.2612 (4)	3.18 (14)	2.93 (15)	2.88 (12)	0.95 (12)	-0.21 (12)	-0.57 (13)
Al(2)	0.3427 (4)	0.7409 (3)	0.5130 (3)	2.74 (14)	2.82 (13)	2.87 (14)	0.65 (11)	0.10 (11)	-0.14 (12)
C(1)	0.2707 (28)	-0.0477 (29)	0.0287 (28)	5.10 (47)					
C(2)	0.2892 (20)	0.1048 (21)	0.0438 (20)	2.82 (31)					
C(3)	0.2366 (22)	0.2066 (24)	-0.0671 (23)	3.03 (35)					
C(4)	0.1681 (26)	0.1623 (28)	-0.1974 (26)	3.44 (43)					
C(5)	0.1563 (24)	0.0088 (25)	-0.2113 (24)	3.77 (38)					
C(6)	0.2056 (24)	-0.0874 (25)	-0.0978 (24)	3.74 (38)					
C(1*)	0.2925 (25)	0.0260 (26)	0.0467 (25)	4.17 (40)					
C(2*)	0.2807 (22)	0.1729 (24)	0.0005 (23)	2.66 (36)					
C(3*)	0.2079 (27)	0.2080 (29)	-0.1375 (27)	2.72 (46)					
C(4*)	0.1501 (20)	0.0849 (21)	-0.2246 (20)	2.09 (31)					
C(5*)	0.1700 (20)	-0.0594 (22)	-0.1679 (21)	2.62 (31)					
C(6*)	0.2445 (26)	-0.0877 (27)	-0.0326 (26)	4.58 (42)					
Complex B									
Pd	0.0139 (1)	-0.1119 (1)	0.0121 (1)	4.63 (6)	2.37 (6)	4.84 (6)	-0.20 (4)	-3.50 (5)	0.24 (4)
Cl(1)	0.0484 (4)	-0.3241 (4)	0.0295 (3)	4.09 (16)	2.27 (17)	3.94 (14)	0.27 (12)	-2.30 (13)	0.19 (15)
Cl(2)	-0.2492 (5)	-0.4119 (6)	0.1469 (4)	5.02 (23)	6.04 (30)	5.05 (23)	-1.70 (21)	-3.20 (21)	1.35 (19)
Cl(3)	-0.1655 (5)	-0.2673 (5)	0.2725 (3)	7.18 (30)	4.50 (27)	3.57 (18)	0.25 (21)	-2.46 (20)	-0.89 (22)
Cl(4)	-0.0624 (5)	-0.5627 (5)	0.1857 (4)	7.64 (30)	3.08 (22)	5.49 (23)	0.39 (18)	-4.53 (23)	0.54 (18)
Al	-0.1112 (5)	-0.3934 (5)	0.1639 (3)	4.15 (22)	2.64 (25)	3.27 (19)	-0.17 (15)	-2.09 (18)	0.41 (21)
C(1)	0.0106 (18)	0.1168 (15)	0.1088 (14)	4.32 (81)	2.89 (84)	4.18 (73)	0.30 (54)	-2.15 (65)	-0.36 (54)
C(2)	0.0275 (20)	-0.0034 (16)	0.1209 (14)	6.03 (103)	2.98 (78)	4.40 (63)	-0.24 (79)	-3.29 (79)	0.73 (58)
C(3)	0.1354 (21)	-0.0622 (20)	0.0512 (19)	6.57 (115)	3.46 (90)	10.22 (159)	0.75 (75)	-7.19 (124)	-0.20 (88)
C(4)	0.2238 (23)	-0.0089 (21)	-0.0348 (15)	7.63 (131)	5.40 (116)	4.34 (81)	2.82 (90)	-4.33 (93)	-2.00 (74)
C(5)	0.2084 (19)	0.1094 (19)	-0.0493 (15)	4.18 (81)	5.55 (116)	5.10 (90)	1.77 (69)	-3.26 (76)	-0.99 (70)
C(6)	0.1079 (15)	0.1784 (16)	0.0225 (12)	3.58 (65)	3.18 (75)	4.31 (49)	-0.03 (49)	-2.87 (58)	-0.18 (52)

ticular structural disorder (Figure 1). The structure was then refined by four cycles of least-squares refinement using a total of 2463 (1397 nonzero) reflections. The final parameters, both geometric and thermal, of all nonhydrogen atoms are reported in Table II. The dis-

Discussion on the Two Structures

(a) **Benzene-to-Metal Coordination.** Although complexes A and B are analogous from both the chemical and the structural points of view, the type of metal-

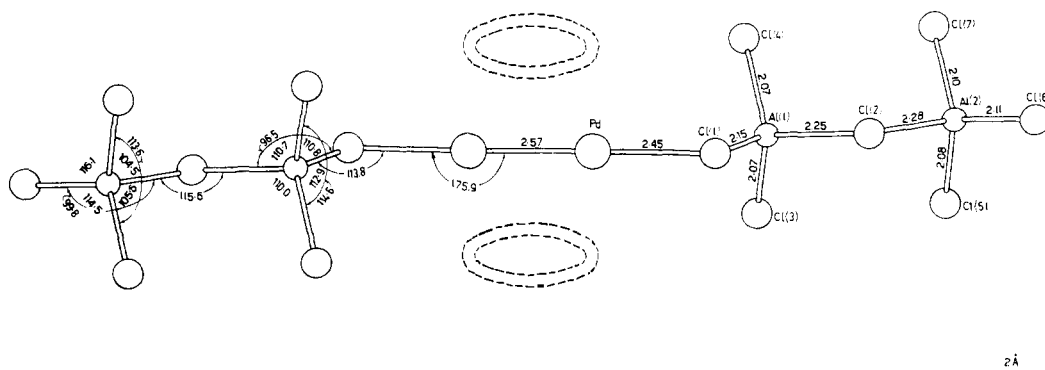


Figure 3. Molecular projection of the A complex; the benzene ring is not shown in detail. The standard deviations of bond lengths (\AA) and angles (deg) are given in Table III.

agreement index R equals 0.091 for the 1397 reflections observed, and 0.143 when nonobserved reflections are included.¹⁵ Figures 4 and 5 show the geometric parameters of the molecule, and Table III lists the average standard deviations for the various types of atomic parameters, bond lengths, and angles.

benzene coordination is considerably different in the two cases. First of all, the benzene ring in A exhibits at least two different orientations with respect to the Pd-Pd axis, neither of which is similar to the single orientation observed in B. Moreover, in the first case, the center of each ring is shifted by only 0.18 \AA from the

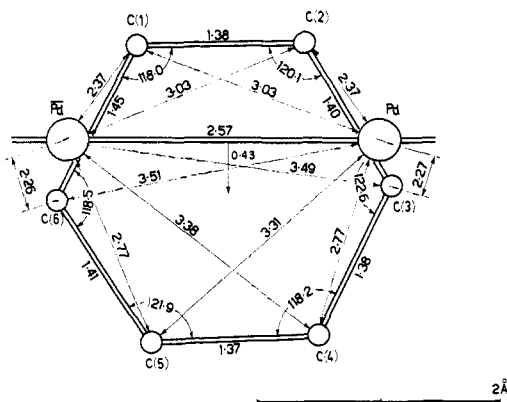


Figure 4. The arene-to-metal coordination in complex B, in a view perpendicular to the average plane of the benzene ring. For the standard deviations of the interatomic distances (Å) and bond angles (deg), see Table III.

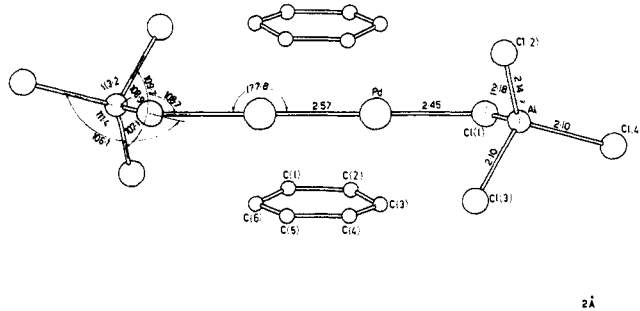
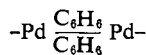


Figure 5. Molecular projection of the B complex. See Table III for the esd's.

projection of the molecular center of symmetry (see Figure 2), whereas, in the second case, such a shift is 0.43 Å (see Figure 4). Referring to these two figures, in the case of complex B, the symmetry of the molecular core



is well described by the D_{2h} group; in the case of complex A, neither orientation observed for the benzene ring is in agreement with such a symmetry group.

Table III. Average Standard Deviations for the Different Types of Bond Lengths (Å) and Angles deg

	Complex A	Complex B
Pd-Pd	0.013 ^a	0.013 ^a
Pd-Cl	0.013	0.013
Pd-C	0.032	0.024
Al-Cl	0.016	0.015
C-C	0.047	0.035
Pd-Pd-Cl	0.5	0.5
Pd-Cl-Al	0.6	0.5
Al-Cl-Al	0.6	
Cl-Al-Cl	0.5	0.5
C-C-C	1.5	1.0

^a The magnitude of this standard deviation is entirely dominated by the inaccuracy in the determination of the unit cell dimensions.

Nevertheless, if the two orientations are considered together, the same local symmetry as in B is observed (*i.e.*, the two benzene orientations are mirror images with respect to a plane orthogonal to the Pd-Pd bond). In our opinion, such differences may hardly be inter-

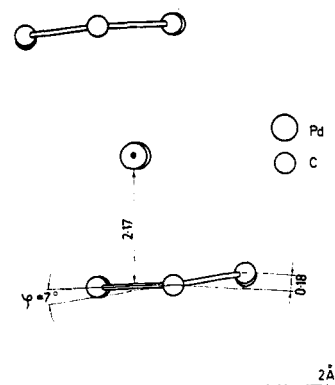


Figure 6. Two projections of a part of the molecule of complex B, showing the distortion of the plane of the benzene ring. The upper projection is seen along the C(3)-C(6) axis, the lower perpendicular to the average ring plane. Distances are in Å; angles in deg.

preted on the basis of the electronic requirements of the Pd atoms and are likely to be attributed to packing forces. Owing to their relative weakness, this type of arene-metal coordination does not seem to be characterized by any sharp minimum of configurational energy.

With particular reference to the more clearly defined structure of B, examination of both coordination geometry and Pd-C distances indicates that four C atoms of each benzene ring are more strongly coordinated to the metal atoms (see Figure 4) than the remaining two C atoms. In the case of A, the existence of a shift of the center of each benzene ring with respect to the projection of the molecular center (Figure 2) still seems to indicate that not all C atoms are equally involved in the coordination with the metal. By assuming, as a first hypothesis, that in the case of B only the C(6), C(1), C(2), and C(3) atoms are bonded to the metal (Figure 6), each ring may be formally assumed to act as a conjugated diene group, in the *cis* conformation, π -coordinating two palladium atoms. The valence shell of the Pd atom should therefore contain 16 electrons, as is the case with many other palladium complexes.¹⁶

Although the average standard deviation of the C-C bond lengths (0.035 Å, see Table III) is too high to supply a proof for the proposed scheme, structural evidence for the reduced aromaticity of the benzene ring is given by its deviation from planarity. (As shown in Figure 6 a dihedral angle of $\sim 7^\circ$ is formed by the two planes defined by C(6)-C(1)-C(2)-C(3) and by C(6)-C(5)-C(4)-C(3).) In spite of the rather high standard deviations, the distortion observed seems reliable since it preserves the local mirror symmetry of the



(16) See, *e.g.*, A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965); R. Mason and D. R. Russell, *Chem. Commun.*, 182 (1965).

group. The hollow part of the benzene ring points *to-ward* the palladium atoms, unlike the case of other arene-metal complexes in which the arene group also acts substantially as a coordinating diene.¹⁷ This may be explained as follows. Let us assume a $d_{\gamma}sp^2$ square-planar hybridization for each palladium atom. A pair of opposite lobes will point along the Cl-Pd-Pd direction, while the other pair will overlap with the π -electron clouds of two C=C bonds belonging to different benzene rings. These four hybrids, involving the $4d_{x^2-y^2}$ orbital, will be electronically filled, whereas the $4d_{z^2}$ orbital, whose z lobes are parallel to the mean plane of the benzene rings, may be empty (we may recall that the compound is diamagnetic, and that the Pd electron configuration, according to the scheme given above, has two electrons short of the Xe configuration). The orientation of the d_{z^2} orbital is such that it may receive part of the π -electron density of the formally uncoordinated C atoms (see Figure 6); therefore, the distortion from planarity of the benzene ring may be connected with the tendency to improve the overlap between the orbitals involved.

As may be seen from Figure 2 with regard to complex A, the most probable metal-to-ring coordination involves an unsymmetrical bonding of a benzene ring, in either orientation, with the two Pd atoms, one of which should be coordinated to an allylic portion of the ring, and the other to a C-C bond. Actually, the steric picture of the benzene rings in complex A probably should be considered as an average deriving from relatively wide thermal oscillations of the benzene rings around their centers. Low-temperature X-ray analysis may supply more definite indications about the metal-to-benzene coordination in this complex.

The comparative analysis of the bond distances and angles around the palladium atoms points out the substantial analogy between A and B, as far as the non-benzene atoms are concerned. The Pd-Pd bond distance observed in both cases (2.57 Å) is markedly lower than the minimum value previously observed for such a bond (in metallic Pd: 2.75 Å).¹⁸ The Pd-Cl (bridge) distance (2.45 Å) is the same in the two complexes, and approaches those distances observed in other cases.¹⁶ The shortest Pd-C distances (2.20–2.25 Å) are similar, and not very different from those observed in other palladium complexes.¹⁶

Table IV reports the shortest packing distances for both compounds. The absence of short (<4 Å) C...C contact in complex A, compared with B, seems to be balanced by shorter C...Cl distances. The figures reported for Cl...Cl are close to the sum of the usually accepted van der Waals radii (3.60 Å).¹⁹ As expected, the shortest C...Cl distances are approximately directed at right angles with the average plane of the ring (compare these figures with the corresponding sum of the van der Waals radii, assuming for carbon 1.7 Å, derived from the structure of graphite).

(b) The Coordination around Chlorine and Aluminum Atoms. From the examination of the Al-Cl bond

(17) M. R. Churchill and R. Mason, *Proc. Chem. Soc.* 365 (1963).

(18) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 282.

(19) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

Table IV. Shortest Intermolecular Distances (Å) for the Two Complexes

	A	B
C...C	4.00	3.72
C...Cl	3.36	3.41
Cl...Cl	3.54	3.62

lengths in both complexes (see Figures 3 and 5) it appears that the bridge bonds are longer than the non-bridge ones. Moreover, in agreement with Sidgwick and Powell's rule on the repulsion among valence shell electron pairs, the Cl-Al-Cl angle has the lowest value when both chlorines are bridging atoms (96.5°, complex A; see Figure 3), intermediate values when only one of them is a bridging atom (average value over the two complexes = 107.7°), and the highest values if both chlorine atoms are simply coordinated (average value over the two complexes = 113.3°).

Interestingly enough, however, the Al-Cl(-Pd) bridge bond lengths observed in the two complexes (2.15 and 2.18 Å for A and B, respectively) are markedly lower than the other Al-Cl bridge bond lengths (2.25 and 2.28 Å, see complex A; compare also with 2.25–2.26 Å found for $(AlCl_2CH_3)_2$).²⁰ We tried to interpret this apparent discrepancy, and the main geometrical features of the coordination around the Al and Cl atoms, from a qualitative examination of the most probable type of hybridization of such atoms. First of all, by attributing hybridization chiefly of the sp type to simply bonded chlorine atoms and an unsymmetrical sp^2 hybridization to bridging atoms, the higher length of the bridge bonds may be explained at once by the wider extension of the orbitals having higher p character. Furthermore, since the dsp^2 orbital of palladium which points toward the chlorine atom is no doubt rather widely extended, the corresponding orbital of chlorine will tend to increase its extension to optimize the overlap, increasing its p character. Consequently, the other orbital of the atom, pointing toward aluminum, will be characterized by a relatively high s character, and the Al-Cl distance will be lower than that observed in Al-Cl-Al bridges, where the two orbitals of chlorine may be more or less equivalent. An interpretation of this type is fully consistent with the experimental data, if hybridization about tetrahedrally coordinated aluminum atoms is examined. In order to obtain the best overlap with the corresponding chlorine orbitals, the aluminum sp^3 orbitals will increase their p character on the bridge bonds, with a corresponding decrease on the others; in this way, the Cl-Al-Cl angles are increased or decreased as predicted by the Sidgwick-Powell rule. Finally, the averages of the four Al-Cl distances from each of the three crystallographically independent Al atoms (Al_1 and Al_2 for A; Al for B) are very similar: 2.135 (Al_1); 2.142 (Al_2); 2.130 Å (Al). It seems that this finding is qualitatively connected with the fact that, whatever is the Al atom, its four hybrid orbitals must contain, on the average, 25% s and 75% p character.

(20) G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).