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CYCLOMETALLATION

V. MOLECULAR STRUCTURES OF ACETATE-BRIDGED DIMERS OF A 2-ARYLPYRIDINE AND A 2,6-DIARYLPYRIDINE CYCLOMETALLATED BY PALLADIUM(II)

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Summary

The crystal and molecular structures of dimeric cyclopalladated acetato(OAc)-bridged complexes of a 2-arylpyridine (**1**) and a 2,6-diarylpyridine (**2**), $[Pd(\mathbf{1})OAc]_2$ (**3**) and $[Pd(\mathbf{2})OAc]_2$ (**4**) have been determined by X-ray diffraction. In each, two planar acetates, nearly perpendicular to each other, *cis*-bridge two Pd^{II} atoms, while the other two square planar sites on each metal are occupied by the cyclometallated aryl-substituted pyridine. The two metal coordination planes are in near parallel registry with one another, giving a "boat" molecule shape of exact (**3**) or near (**4**) two-fold symmetry. The non-bonding Pd · · · Pd distance (δ) strongly correlates with the angle (α) subtended by the metal coordination planes, which in turn seems related to the steric requirements of the non-bridging ligands. In **3**, with the planar nitrophenylpyridine ligand, α 25.7° and δ 2.822(6) Å, the shortest Pd · · · Pd distance yet observed in dimers of this type. The Pd–C lengths, 1.94 Å in **3** and 1.944 Å in **4**, are significantly shorter than the calculated length, 2.05 Å, suggesting partial multiple bond character in these shortest Pd–C (aryl) bonds so far observed. Pd–N bond lengths are near expected single bond lengths. Failure of *trans*-dimetallation to occur in **4**, analogous to that recently observed with certain 2,6-dialkylpyridines or to the tridentate behavior of terpyridine in $[Pd\ terpy\ X]^+$ compounds, appears due to a combination of the shortened Pd–C bond in the first-formed metallated ring and the larger constraining angles (near 120° for sp^2 carbons) in the remaining (unmetallated) ring.

Introduction

A one page report [1] of the molecular structure of π-allyl palladium acetate pictured it as an acetato-bridged dimer and suggested that the Pd · · · Pd distance of 2.94 Å (0.3–0.4 Å shorter than in $[Pd(NH_3)_4][PdX_4]$, with $X = Cl^-$, Br^-, or SCN^-) represented a metal–metal bond. A decade later the structure of a second acetato-bridged palladium-(II) dimer, di-μ-acetato-bis[(2-methylallyl-3-norbornyl) pal-

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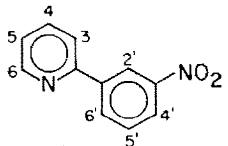
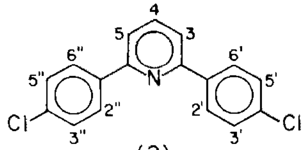
ladium(II)]$_2$ was reported [2], in which a Pd · · · Pd distance of 2.960 Å was found and considered to represent "a rather strong interaction... between the two Pd ions". Two different Pd–O distances (2.198 and 2.106 Å) were taken as evidence of a strong *trans* influence of the carbon atom of the norbornyl entity. The first acetato-bridged dimer of cyclometallated palladium(II) appears to be sym-*trans*-di-μ-acetato-bis[*o*-(t-butyl-*o*-tolylphosphino) benzyl] dipalladium(II), in which a sterically hindered phosphorus coordinates to the metal and internal metallation has occurred at a tolyl-methyl carbon [3]. The very long Pd · · · Pd distance of 3.413 Å



(1)



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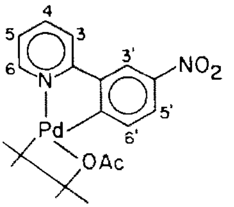
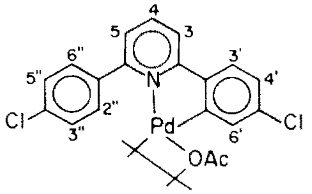


(3)



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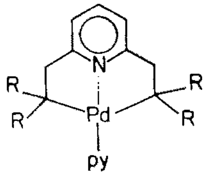

(R = CO_2CH_3 or $CO_2C_2H_5$;

py = pyridine)

(5)

"is held to be non-bonding", and is attributed to the "intramolecular steric overcrowding between the bulky phosphine ligands". The similar Pd–O lengths (2.120 and 2.138 Å) suggest there is little difference in the *trans* influences of a benzyl carbon and a phosphorus. The dimer bis(μ-acetato)-dichlorobis(dimethylphenylphosphine) dipalladium(II) (which crystallizes with 1/2 $CHCl_3$ per mol), while acetato-bridged, does not involve cyclopalladation. However the boat conformation of the bridging acetates does bring the palladium atoms to within 2.944 Å of each other; but here the authors [4] state that there "is no direct interaction between the two metal ions". A greater *trans* effect of phosphine compared to chloride seems to be monitored in the respective Pd–O lengths *trans* to these atoms, 2.12(mean) and 2.03(mean) Å. Recently the crystal structures were reported [5] for two other dimeric cyclopalladated products with acetate bridges: [Pd(2-*p*-tolylbenzthiazole)OAc]$_2$ and [Pd(2-*p*-tolylbenzoxazole)OAc]$_2$. The Pd · · · Pd distances are 2.871 and 2.842 Å, respectively, and "are regarded as nonbonding". It is interesting that in each compound the cyclometallation involves N, C bonding, rather than the other possibilities of S, C and O, C, respectively. The *trans*-lengthening influence of a bonded aryl carbon relative to that of a coordinated nitrogen is clearly illustrated by the Pd–O lengths trans to these atoms (e.g., 2.139 vs. 2.049 Å and 2.129 vs. 2.052 Å, in the two compounds).

We prepared and studied by IR and NMR a number of cyclopalladated compounds of 2-arylpyridines [6,7] and 2,6-diarylpyridines [8] and we determined [9] by X-ray diffraction the structure of $[Rh(\mathbf{1})_2Cl]_2$.

We now report the X-ray crystal structures of two dimeric acetato-bridged cyclopalladated complexes:

bis(μ-acetato-*O*: *O′*)-bis[4′-nitro-2′-(2-pyridyl)phenyl-*N*]dipalladium(II), **3**, and bis(μ-acetato-*O*: *O′*)-bis[5′-chloro-2′-{6-(4″-chlorophenyl)-2-pyridyl}-phenyl-*N*]dipalladium(II), **4**; and discuss the relevance of these structures to those mentioned above (both Pd^{II} and Rh^{III}) and to some questions concerning metal- ligand bonding in cyclometallated compounds. The existance of planar palladium(II)-terpy compounds, where terpy = 2,6-di(2′-pyridyl)pyridine, and in particular the crystal structure [10] of [Pd terpy Cl] Cl which proves coordination via all three nitrogens, was the impetus to see if the structurally related 2,6-diarylpyridine (**2**) could likewise serve to *trans*-dimetallate. The only previous success [11] at *trans*-dimetallation produced compounds such as **5**, in which the metallating carbons are sp^3. Efforts [8] to metallate the second ring in **4** were unsuccessful and so it was of interest to see if the detailed structure of the monometallated product (**4**) could help explain this failure.

Experimental

Complexes **3** and **4** were prepared as previously described [6,8]. A red-orange crystal of **3** was mounted in air on a glass fiber and mounted in random orientation on an Enraf-Nonius CAD4 automated diffractometer. Crystalline lattice characterization and data collection were as described in detail elsewhere [12] except that an empirical (ψ-scan) absorption correction was applied to each reflection. The relevant crystal data are listed in Table 1.

A total of 1644 observed reflections were used to calculate the Patterson and successive Fourier difference maps, from which all 20 non-hydrogen atoms in one-half of the two-fold symmetric molecule were located. In addition, all hydrogen atoms except those of the methyl group were located; the methyl hydrogen positions were calculated assuming sp^3 hybridization, and were held fixed relative to the methyl carbon position. In the weighted full matrix least squares refinement, all non-hydrogen atoms were treated anisotropically, hydrogen atoms were treated isotropically. For the final structural model ($R = 0.029$) no parameter shifted more than 0.3σ, and no residual electron density greater than 0.5 $eÅ^{-3}$ was observed on a difference map.

Data were also collected for **4**. A yellow crystal of **4** containing 50 mol% chloroform molecules of solvation, was sealed in a thin walled glass capillary under an atmosphere of chloroform. Data were collected and treated as for **3**. However, because of the nearly orthorhombic lattice, and also because of the symmetry of the molecule itself (vide infra) special care was taken to characterize the lattice and

TABLE 1

CRYSTALLOGRAPHIC DATA

Formula	(3) $(PdC_{13}H_{10}N_2O_4)_2$	(4) $(PdC_{19}H_{13}NO_2Cl_2)_2 \cdot CHCl_3$
Formula weight	729.3	1048.6
Crystal size (mm)	0.12 × 0.20 × 0.32	0.12 × 0.32 × 0.52
Crystal system	monoclinic	monoclinic
Space group	$I2/c$ [a]	Pn
D_c (g cm^{-3})	1.811	1.742
Z(molecules/cell)	4	2
a (Å)	14.300(3)	11.776(2)
b (Å)	9.939(1)	7.538(2)
c (Å)	18.822(2)	22.525(3)
β (°)	91.01(1)	90.25(1)
V (Å^3)	2674.8(1)	1999.5(1)
λ(Mo-K_α) (Å)	0.71069	0.71069
Data collection	ω/2θ	ω/2θ
Intensities: measured	2048	3500
$I > 3\sigma(I)$	1644	3177
μ(Mo-K_α) (cm^{-1})	13.8	13.9
Minimum transmission	91.5%	84.0%
Variables	186	281
R	0.029	0.031
R_w	0.050	0.042

[a] Space group $I2/c$ is an alternate setting of $C2/c$, with general equivalent positions $(0,0,0; 1/2,1/2,1/2) + x,y,z; \bar{x},y,z; x+1/2,y,z; x,y+1/2,z+1/2$.

TABLE 2

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $(PdC_{13}H_{10}N_2O_4)_2$

Atom	x	y	z	B [a]
Pd	1.65306(2)	1.11557(4)	1.01288(2)	3.332(2)
O(1)	1.7031(3)	1.2513(4)	1.0933(2)	5.3(1)
O(2)	1.6475(3)	1.2710(4)	0.9431(2)	4.6(1)
O(3)	1.4374(4)	0.7120(6)	0.7660(2)	7.0(2)
O(4)	1.4742(4)	0.5637(5)	0.8445(3)	6.7(2)
N(1)	1.6481(3)	0.9555(4)	1.0785(2)	3.6(1)
N(2)	1.4762(4)	0.6797(6)	0.8217(3)	5.2(2)
C(1)	1.6022(3)	0.9851(5)	0.9464(2)	3.2(1)
C(2)	1.5776(4)	1.0079(6)	0.8733(2)	4.0(1)
C(3)	1.5370(4)	0.9090(6)	0.8335(3)	4.3(1)
C(4)	1.5216(4)	0.7833(6)	0.8624(3)	4.1(1)
C(5)	1.5463(4)	0.7548(6)	0.9350(3)	4.3(1)
C(6)	1.5873(4)	0.8562(5)	0.9735(3)	3.5(1)
C(7)	1.6136(3)	0.8401(5)	1.0498(2)	3.4(1)
C(8)	1.6045(4)	0.7254(6)	1.0906(3)	4.9(2)
C(9)	1.6302(5)	0.7305(7)	1.1616(3)	5.2(2)
C(10)	1.6668(5)	0.8452(8)	1.1901(3)	5.4(2)
C(11)	1.6741(4)	0.9581(6)	1.1467(3)	4.3(1)
C(12)	1.7174(4)	1.3037(5)	0.9040(3)	4.1(1)
C(13)	1.7030(6)	1.4167(8)	0.8537(4)	6.9(2)

[a] Equivalent isotropic temperature factor: International Tables for X-Ray Crystallography, Vol. 4, p. 316.

TABLE 3

ATOMIC POSITIONAL PARAMETERS AND ISOTROPIC THERMAL PARAMETERS FOR $(PdC_{19}H_{13}NO_2Cl_2)_2 \cdot CHCl_3$

Atom	*x*	*y*	*z*	*B*
Pd(1)	0	0.46119(5)	0	2.901(7) [a]
Pd(2)	−0.01543(5)	0.07695(6)	0.00618(3)	3.119(8) [a]
Cl(1)	0.0662(3)	0.4827(5)	−0.2493(1)	7.18(7) [a]
Cl(2)	0.0268(3)	0.6883(4)	0.2950(1)	7.33(6) [a]
Cl(3)	−0.3814(3)	0.0654(5)	0.1691(1)	8.16(7) [a]
Cl(4)	0.4620(2)	−0.1898(4)	−0.1529(1)	7.20(6) [a]
Cl(5)	0.8627(3)	0.5239(4)	−0.3903(1)	7.34(7) [a]
Cl(6)	0.7743(4)	0.2058(5)	−0.4457(2)	10.03(10) [a]
Cl(7)	0.8021(4)	0.2241(5)	−0.3202(2)	9.48(9) [a]
O(1)	0.0643(4)	0.4018(6)	0.0893(2)	3.82(9)
O(2)	0.1650(4)	0.4179(7)	−0.0255(2)	4.05(9)
O(3)	0.1626(4)	0.1231(7)	−0.0154(2)	3.95(9)
O(4)	0.0358(4)	0.1116(7)	0.0930(2)	4.20(9)
N(1)	−0.1653(5)	0.5338(7)	0.0137(2)	3.19(9)
N(2)	−0.0822(5)	0.0230(8)	−0.0762(3)	3.5(1)
C(1)	−0.0451(6)	0.4898(9)	−0.0826(3)	3.3(1)
C(2)	0.0236(7)	0.4746(10)	−0.1320(4)	4.0(1)
C(3)	−0.0229(7)	0.4952(11)	−0.1880(4)	4.5(1)
C(4)	−0.1362(8)	0.5257(13)	−0.1978(4)	5.3(2)
C(5)	−0.2068(8)	0.5385(11)	−0.1483(4)	4.8(2)
C(6)	−0.1622(6)	0.5215(10)	−0.0916(3)	3.6(1)
C(7)	−0.2287(6)	0.5383(9)	−0.0368(3)	3.6(1)
C(8)	−0.3438(8)	0.5548(12)	−0.0363(3)	5.2(2)
C(9)	−0.3988(8)	0.5726(12)	0.0171(4)	5.5(2)
C(10)	−0.3361(8)	0.5792(12)	0.0683(4)	5.3(2)
C(11)	−0.2190(7)	0.5594(10)	0.0668(3)	3.9(1)
C(12)	−0.1518(6)	0.5796(9)	0.1224(3)	3.4(1)
C(13)	−0.0646(7)	0.7051(10)	0.1256(3)	4.0(1)
C(14)	−0.0119(8)	0.7417(11)	0.1781(4)	4.8(2)
C(15)	−0.0430(7)	0.6490(11)	0.2281(4)	4.5(1)
C(16)	−0.1268(8)	0.5207(12)	0.2265(4)	5.2(2)
C(17)	−0.1837(7)	0.4915(11)	0.1734(4)	4.4(1)
C(18)	0.0690(6)	0.2558(8)	0.1138(3)	3.3(1)
C(19)	0.1178(8)	0.2444(11)	0.1761(4)	4.8(2)
C(20)	0.2104(7)	0.2670(9)	−0.0256(3)	3.6(1)
C(21)	0.3357(8)	0.2599(11)	−0.0415(4)	4.9(2)
C(22)	−0.1739(6)	0.0566(8)	0.0295(3)	3.2(1)
C(23)	−0.2134(7)	0.0661(10)	0.0879(4)	4.3(1)
C(24)	−0.3289(8)	0.0601(12)	0.0970(4)	5.0(2)
C(25)	−0.4066(8)	0.0506(13)	0.0501(4)	5.4(2)
C(26)	−0.3663(8)	0.0467(12)	−0.0067(4)	5.1(2)
C(27)	−0.2488(7)	0.0484(10)	−0.0168(3)	3.9(1)
C(28)	−0.1984(6)	0.0338(9)	−0.0765(3)	3.7(1)
C(29)	−0.2592(7)	0.0337(11)	−0.1287(4)	4.7(2)
C(30)	−0.2047(9)	0.0149(14)	−0.1824(4)	5.6(2)
C(31)	−0.0887(8)	−0.0022(13)	−0.1820(4)	5.1(2)
C(32)	−0.0293(6)	0.0008(10)	−0.1278(3)	3.8(1)
C(33)	0.0942(7)	−0.0396(10)	−0.1311(3)	3.8(1)
C(34)	0.1450(6)	−0.1615(10)	−0.0937(3)	4.0(1)
C(35)	0.2569(8)	−0.2095(11)	−0.1004(4)	4.6(1)
C(36)	0.3199(7)	−0.1314(12)	−0.1442(4)	4.7(2)
C(37)	0.2743(8)	−0.0057(13)	−0.1815(4)	5.1(2)
C(38)	0.1608(7)	0.0405(10)	−0.1742(3)	4.1(1)
C(39)	0.7719(8)	0.3436(12)	−0.3837(4)	5.2(2)

[a] Equivalent isotropic temperature factor: International Tables for X-Ray Crystallography, Vol. 4, p. 316.

space group. No lattice or space group with more symmetry than monoclinic-*Pn* is consistent with the data; presumably this low symmetry results from packing distortion of the two parachlorophenyl substituents and also because only one chloroform molecule per dimer is included in the lattice.

Patterson, Fourier, and subsequent full matrix least squares techniques utilized 3177 observed reflections to locate and refine the positions of all 54 non-hydrogen atoms in **4** and the chloroform molecules. Only the Pd and Cl atoms were treated anisotropically, while all H, C, N, and O atoms were treated isotropically. All hydrogen atoms were fixed in calculated positions relative to their attached atoms. Refinement proceeded smoothly to $R = 0.031$ with no correlations above 0.5, and the final difference map showed a maximum residual electron density of 0.55 eA^{-3} associated with the Pd atom.

The atomic scattering factors (Cromer and Mann [13]) were corrected for dispersion [14]. Atomic positional parameter are listed in Tables 2 and 3, while bond lengths and angles are shown in Figs. 2 and 4. Tables of structure factors and anisotropic thermal parameters are available from the authors upon request.

Discussion of the structures

Both **3** and **4** have a central geometry (see Figs. 1 and 3) similar to that observed in other bis(μ-acetato)-dipalladium(II) complexes [1,2,4,5]. The approximate features are as follows: two acetates *cis*-bridge two palladium atoms, while the other two square planar coordination sites on each metal are occupied by substituted phenylpyridine bidentate ligands. The planar acetate bridging groups are nearly perpendicular to one another and to the metal coordination planes, but the two metal coordination planes are in nearly parallel registry with one another. The molecular shape is thus that of a boat of exact (**3**) or near (**4**) two-fold symmetry.

There are specific distortions in the geometry described above which are fairly consistent over most known structures, including the two reported herein. For example, the non-bonding Pd···Pd distance (δ) is strongly correlated * with the angle (α) subtended by the metal coordination planes, which in turn seems to be related to the steric requirements of the non-bridging ligands. Thus, in **3**, with the highly planar nitrophenylpyridine ligand, α 25.7° and δ 2.822(6) A, the *shortest Pd···Pd distance yet observed in dimers of this type*. In **4** with the bulky parachlorophenyl substituents, the dihedral angle is opened slightly (α 25.9°) and the acetate bridge stretched (see Figs. 2 and 4) so that δ 2.906(1) A. The greatest angle/distance yet observed is 48°/3.413(1) A to accommodate a tetrahedral, bulky substituted phosphorus ligand [3]. If the only steric requirements were those of symmetrically bridging acetate groups, the "unstressed" Pd···Pd distance would be about 2.7 A [15]. However, in most known dimers of this type, the acetate bridges do not span the metals symmetrically, due in part to the stresses imposed by bulky ligands, and also to *trans* effects (vide infra) at the metal. Thus, the O-C-O angle is correlated to the Pd···Pd distance, and one Pd–O bond is consistently longer than the other. Bridge asymmetry in **4** may also be enhanced by the hydrogen bond formed between the chloroform solvate molecule and O(1) of the acetate bridge

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* Correlation coefficient 0.875, sum of squared residuals (linear least squares) 0.059.

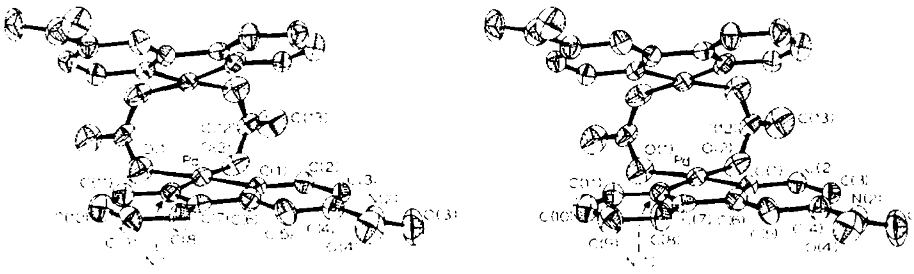

Fig. 1. Stereodiagram of $(PdC_{13}H_{10}N_2O_4)_2$ (3).

(O(1)···C(20) 3.16 Å, O(1)–H 2.20 Å, O(1)–H–C(20) 145°). Chloroform-oxygen hydrogen bonding is a well established phenomenon in the solid state [17,18].

Details of the geometries of **3** and **4** are set forth below. It is interesting to note that, while the dimer **3** is of exact (crystallographic) two-fold symmetry, the dimer **4** deviates from two-fold symmetry, most notably in the orientation of the free parachlorophenyl ring, probably to accommodate packing forces and a chloroform molecule.

Metal coordination

3: All four coordinated atoms, O(1), O(2), N(1) and C(1), lie within one e.s.d. of the basal plane of a pyramid, at the apex of which is the Pd atom 0.051(1) Å above the plane toward the adjacent Pd atom.

4: Each independent metal atom lies in a mean plane, and the coordinated atoms are situated an average of 0.086(6) Å alternately above and below this plane such that *trans*-coordinated atoms are displaced on the same side of the plane. This "S_4"

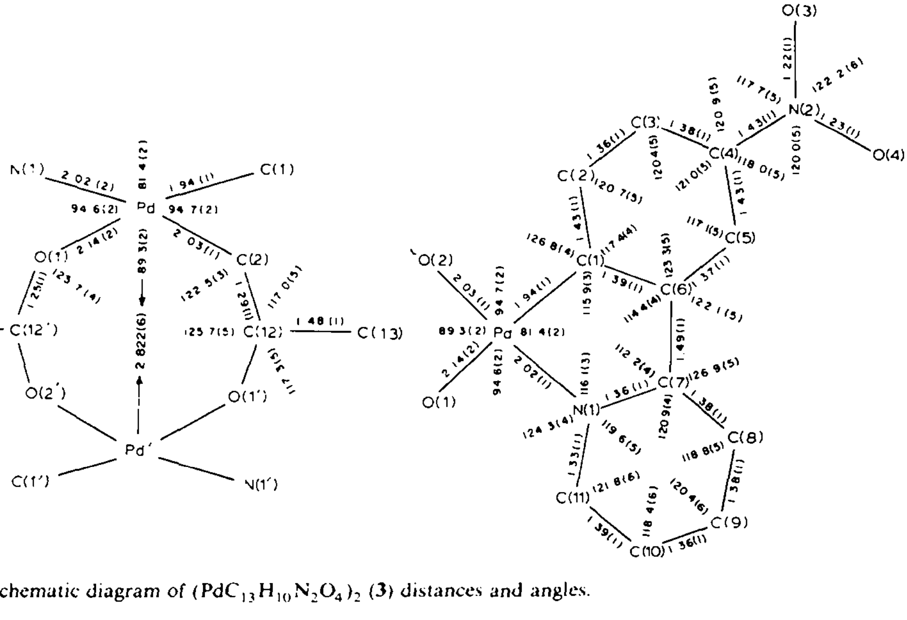

Fig. 2. Schematic diagram of $(PdC_{13}H_{10}N_2O_4)_2$ (3) distances and angles.

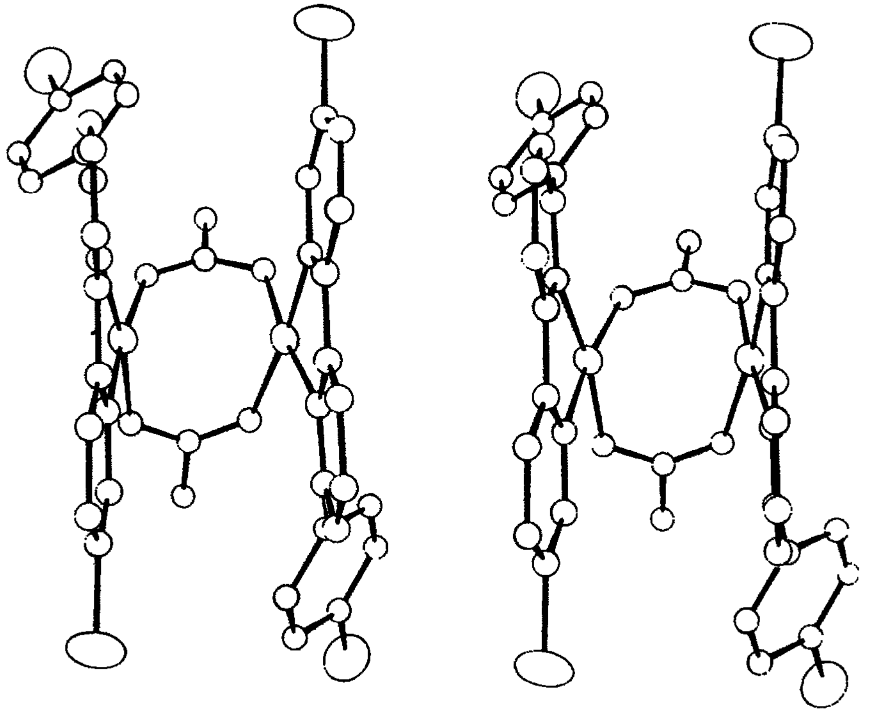

Fig. 3. Stereodiagram of the $(PdC_{19}H_{13}NO_2Cl_2)_2$ (4) dimer as found in crystalline $(PdC_{19}H_{13}NO_2Cl_2)_2 \cdot CHCl_3$.

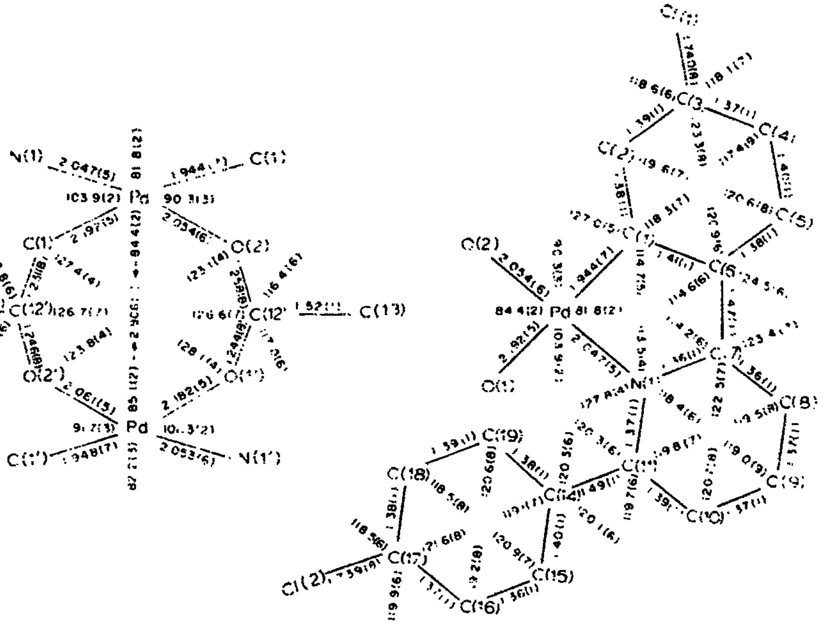

Fig. 4. Schematic diagram of $(PdC_{19}H_{13}NO_2Cl_2)_2$ (4) showing interatomic distances and angles.

distortion is in marked contrast to the "C_{4v}" distortion in **3**. The Pd–C bond lengths, 1.94 Å in **3** and 1.944 Å in **4**, are significantly shorter than the calculated single bond length of 2.05 Å (based on the covalent radius of Pd^{II} 1.31 Å [19] and $C(sp^3)$–$C(sp^3)$ 1.537 Å and $C(sp^3)$–$C(sp^2)$ 1.510 Å [19]), suggesting partial multiple bond character in the Pd–C (aryl) linkages. These appear to be the shortest Pd–C (aryl) bonds thus far observed [5,20], and coupled with proton NMR shift data [6,8], the evidence is strong for palladium-to-aryl π back-bonding. While some of the shortening of the metal–carbon distance might be anticipated in the cyclometallated ring, the 0.1 Å shortening in the Pd–C bonds may be compared to the 0.05 Å shortening found in the Rh^{III}-C(aryl) bond in the related $[Rh(\mathbf{1})_2Cl]_2$ [9]. In the latter, with only t_{2g} electrons, no π back-bonding is expected, although some ligand-to-metal π-electron flow is possible.

A combination of factors may account for the failure of Pd^{II} to dimetallate with 2,6-diarylpyridines. For example, the metal–nitrogen bonds *trans* to each other in [Pd terpy Cl]Cl are slightly longer than single bond length (2.044 and 2.104 Å vs. a calculated 2.01 Å) [10], whereas in **4** the shortened metal–carbon bond (vide supra) implies multiple bonding. Perhaps after this first Pd–C bond forms, and pulls the Pd atom away from the other ring (where *ortho* carbons are now at 2.427 and 2.252 Å), effective metallation is prevented. Furthermore, note that in **5** ($R = CO_2C_2H_5$) the cyclometallated (mean) ring angles Pd–C–C and C–C–C, involving sp^3 carbons, are 102.2 and 110.8°, respectively [11], whereas the corresponding ring angles in **4**, involving sp^2 carbons, are 114.7 and 114.6°. These latter angles plus the approximate 120° angles (e.g., C(11)–C(14)–C(19), Fig. 4) which constrain the unmetallated aromatic ring system, coupled with the shortened Pd–C (aryl) bond, must all combine to prevent dimetallation.

The Pd–O distances *trans* to the carbons are 2.14 Å in **3** and 2.192 Å in **4**, whereas the Pd–O distances *trans* to the nitrogens are 2.03 Å in **3** and 2.054 Å in **4**. Although some asymmetry in the acetate bridge is expected on other grounds (vide supra), the substantial differences in the Pd–O distances surely also reflect the stronger *trans*-lengthening influence of an aromatic carbon compared to an aromatic nitrogen. Finally, the Pd–N lengths, 2.02 Å in **3** and 2.047 Å in **4**, are only slightly longer than the calculated single bond value of 2.01 Å (based upon Pd^{II} 1.31 Å [20] and $N(sp^2)$ 0.70 Å [21]). In the analogous rhodium compound, $[Rh(\mathbf{1})_2Cl]_2$ a slight lengthening of Rh–N (by 0.05 Å) is found [8].

Acetate bridges

3: The four independent non-hydrogen atoms of the acetate group lie in a plane, and the two acetate planes subtend an angle of 81.6°. The C(12) acetate plane is skewed with respect to the basal planes of the metal coordination polyhedra: 86.4 (Pd) and 76.8° (Pd′).

4: The two independent acetates are planar and subtend an angle of 79.9°. The equivalent skewed angles to the mean planes of the two metal coordination polyhedra are: 88.1°/86.9° and 76.2°/75.5°.

Bidentate phenylpyridyl ligand

Three rings compose this ligand system: the five-member metallocyclic ring (I), the phenyl ring (C(1)–C(6))(II), and the pyridine ring (III). **3**: All three rings are individually planar (within experimental error) and mutually co-planar to within 3°.

The dihedral angles with respect to the basal plane of the metal coordination polyhedron are: (I) 2.3°, (II) 4.6°, (III) 3.7°.

(**4**-average over two independent ligands): Ring I has a perceptible envelope conformation, with Pd at the flap, while rings II and III are planar. Rings II and III subtend an angle of 7.5°, and with respect to the mean plane of the metal coordination polyhedron the dihedral angles are 5.3 (II) and 12.6° (III). Thus, the phenylpyridine system is significantly nonplanar in **4**.

Ligand substituents

3: The only substituent is a nitro group on the phenyl ring *para* to palladium. The four atoms (including C(4)) which define this group lie in a plane which is not quite coplanar with the phenyl ring, but is twisted 13° about the C–N bond.

4: Each of the two phenylpyridyl ligands contains two substituents: (1) chlorine atoms on the phenyl rings *meta* to each palladium are 0.023(4) and 0.042(4) A from the ring plane away from the adjacent metal atom; (2) parachlorophenyl groups *ortho* to the pyridine nitrogen atoms are bent out of the pyridine planes away from the adjacent metals such that the C(14) atoms lie 0.144(7) and 0.180(7) A out-of-plane. In addition, the chlorophenyl ring planes are twisted about the C–C bonds by 52 and 46°.

Chloroform

The chloroform molecule appears normal, with three C–Cl distances of 1.726, 1.726, and 1.740 A (each with σ 0.010 A; average bond length 1.734(7) A) and bond angles 112.7, 110.8 and 110.4° ($\sigma = 0.5$).

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