

STRUCTURAL SYSTEMATICS OF THE ISOMERIC DI- μ -CHLOROBIS(*N,N*-DIALKYL BENZYLAMINE-2,*C,N*)DIPALLADIUM(II) COMPLEXES. THE CRYSTAL STRUCTURES OF THE *ortho*-, *meta*- AND *para*-METHOXY SUBSTITUTED COMPLEXES

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Summary

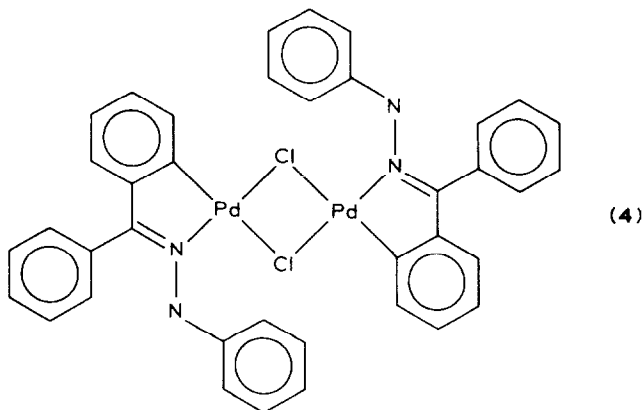
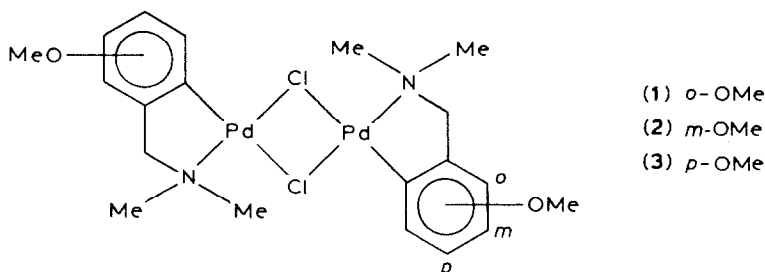
The crystal structures of three isomeric methoxy substituted bis-chloro bridged (*N,N*-dimethylbenzylamine)palladium(II) dimers have been determined by X-ray diffraction. Both the *ortho*-isomer (**1**) and the *meta*-isomer (**2**) are monoclinic, spacegroup $P2_1/c$ with $Z = 2$ in cells of dimensions a 5.7391(7), b 17.794(4), c 10.907(2) Å, β 97.76(1)° (**1**), and a 9.897(1), b 11.178(2), c 10.660(2) Å, β 105.76(1)° (**2**). The four molecules of the *para*-isomer (**3**) crystallize with two molecules of toluene of solvation in a cell of dimensions a 8.403(1), b 20.056(3), c 15.521(2) Å, $\beta = 90.54(1)^\circ$, space group $P2_1/n$. All three complexes have the expected *trans*-related dimeric structures about square planar palladium(II) centres, although **3** does not have the centrosymmetry of **1** and **2**. The Pd–C and Pd–N bond lengths show no significant variation across the series (range 1.967–1.986 Å; mean, 1.977 Å) and (range 2.068–2.075 Å; mean, 2.071 Å), respectively. The Pd–Cl bridge bonds are asymmetric, consistent with the *trans* effect of the Pd–C bond (range, 2.466–2.488 Å; mean 2.476 Å and 2.334–2.341 Å; mean, 2.337 Å).

Introduction

The bis-chloro-bridged palladium(II) dimeric complexes having Pd–C(σ) (sp^2) bonds have been known for some time [1,2]. Conventional structure determinative techniques (NMR and IR) have been used to confirm the *trans* configuration of the

N,N-dialkylbenzylamine moieties in these complexes, while an analogy between the Pd^{II} and Pt^{II} compounds has been drawn [2] from the X-ray structure of the corresponding phenylazophenylplatinum(II) complex [3]. Such an analogy is justified since very little difference exists between the structural features, including the corrected metal–Cl distances for the complex anions in K₂[PtCl₄] and K₂[PdCl₄] [4] and the isostructural di- μ -chlorobis[2-(di-*t*-butylphosphino)-2-methylpropyl]dipalladium(II) and -platinum(II) complexes [5]. To date, however, there has been a paucity of X-ray structural data available for this group of compounds. Extensive comparative data on the monomeric PdCl₂L₂ complexes (L₂ = two unidentate or one bidentate ligand) are presented by Steffen and Palenik [6], but among the systems involving bis-chloro bridges, the majority have Pd–C(π) [7,8,9], Pd–C(σ)(*sp*³) [5,10,11] or Pd–C(π) and C(σ) [12,13,14]. The only other example of a bis-chloro-bridged dimer having only Pd^{II}–C(σ)(*sp*²) bonds is a compound (4) completed in this laboratory.

The isomeric title compounds 1, 2 and 3 reported here provide a series which allowed comparison of structural data, which includes the possible effect of the position of the methoxy group substituent in the aromatic ring upon the Pd–C, Pd–N and Pd–Cl bond lengths. Also of interest is the *trans* influence provided by the coordinated C and N donor groups.



Experimental

Preparation of complexes

Isomeric complexes **1**, **2** and **3** were prepared by the general method described in ref. 2. Crystals of **1** and **2** suitable for an X-ray diffraction study were obtained by slow evaporation of chloroform solutions. For **3**, an uncompromising crystal morphology was obtained from chloroform but excellent crystals were grown from toluene. Preliminary X-ray examination indicated comparable cell volumes for **1** and **2** (1104 Å³ and 1135 Å³ respectively, with 2 dimers per cell) but **3** had a cell volume larger than expected for four dimers (2616 Å³). Elemental analysis of these crystals (found: C, 43.3; H, 4.98; Cl, 10.39%) suggested the possible incorporation of half a mole of toluene per complex dimer (C_{23.5}H₃₂Cl₂N₂O₂Pd₂ calcd.: C, 42.9; H, 4.90; Cl, 10.8%).

Crystal data, X-ray data collection and structure refinement

Table 1 details until cell parameters, data acquisition, structure solution and refinement for complexes **1**, **2** and **3**. Data were corrected for Lorentz and polariza-

TABLE 1
CELL DATA FOR [OMPD], (**1**); [MMPD], (**2**) and [PMPD], (**3**)

	1	2	3
Formula	C ₂₀ H ₂₈ Cl ₂ N ₂ O ₂ Pd ₂	C ₂₀ H ₂₈ Cl ₂ N ₂ O ₂ Pd ₂	C _{23.5} H ₃₂ Cl ₂ N ₂ O ₂ Pd ₂
<i>M</i> _{rel.}	611.8	611.8	658.3
<i>a</i> (Å)	5.7391(7)	9.897(1)	8.403(1)
<i>b</i> (Å)	17.794(4)	11.178(2)	20.056(3)
<i>c</i> (Å)	10.907(2)	10.660(2)	15.521(2)
β (°)	97.76(1)	105.76(1)	90.54(1)
<i>V</i> (Å ³)	1103.9	1135.0	2615.6
<i>Z</i>	2	2	4
ρ_c (g cm ⁻³)	1.841	1.791	1.672
ρ_m (g cm ⁻³)	1.82	1.80	1.70
μ (cm ⁻¹)	18.56	18.05	15.73
λ (Å)	0.7107	0.7107	0.7107
<i>F</i> (000)	608	608	1316
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Data collection</i>			
a. diffractometer	Nicolet R3m	Nicolet R3m	Nicolet R3m
b. radiation	Mo- <i>K</i> _α	Mo- <i>K</i> _α	Mo- <i>K</i> _α
c. 2 θ _{max} (°)	50	50	53
d. unique reflections measured	1603	1496	4700
e. crystal size (mm)	0.25 × 0.12 × 0.12	0.24 × 0.15 × 0.12	0.35 × 0.15 × 0.13
<i>Structure solution, refinement</i>			
a. method used	Direct methods	Direct methods	Heavy atom
b. <i>R</i>	0.026	0.024	0.039
c. <i>R</i> _w	0.030	0.030	0.043
d. <i>w</i> ^a A	0.61	0.51	1.93
B	1.1 × 10 ⁻³	1.6 × 10 ⁻³	5.6 × 10 ⁻⁴
e. data used	1237	1335	3459
f. discrimination	<i>I</i> > 2.5σ(<i>I</i>)	<i>I</i> > 2.5σ(<i>I</i>)	<i>I</i> > 3.0σ(<i>I</i>)

^a *w* = *A*/(σ²*F*_o + *B**F*_o²).

tion effects but not for absorption. The structures of **1** and **2** were solved by the centrosymmetric direct methods of SHELX-76 [16] while for **3**, the Patterson heavy atom method was used. Blocked-matrix least-squares refinement was used, with all non-hydrogen atoms anisotropic, except those of the disordered molecules of solvation in **3**. With **3**, the two toluenes of solvation, which by space group requirements

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2, \times 10^3$) FOR [OMPD] (**1**), [MMPD] (**2**) and [PMPD] (**3**) (U_{eq} is defined as $(U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$)

	1				2			
	x/a	y/b	x/c	U_{eq}	x/a	y/b	z/c	U_{eq}
Pd	1103.0(6)	4707.3(2)	3640.7(3)	31.2(3)	434.7(3)	678.9(3)	3677.3(3)	39.3(3)
Cl	1305(2)	5817(1)	5014(1)	44.5(7)	1694(1)	-304(1)	5565(1)	49.9(6)
N(21)	3098(6)	5154(2)	2366(3)	34(2)	-618(3)	1574(3)	1997(3)	46(2)
C(1)	897(8)	3838(3)	2504(4)	36(3)	2053(4)	851(3)	2923(4)	45(2)
C(2)	2504(9)	3851(2)	1661(4)	37(3)	1789(4)	1616(4)	1842(4)	47(2)
C(21)	4194(9)	4513(3)	1752(5)	44(3)	442(4)	2290(4)	1526(4)	56(3)
C(3)	2592(9)	3271(3)	807(4)	40(3)	2785(4)	1774(4)	1143(4)	53(3)
C(4)	1031(10)	2685(3)	791(5)	48(3)	4024(4)	1150(4)	1519(5)	55(3)
C(5)	-566(10)	2671(3)	1622(5)	49(3)	4314(4)	399(4)	2604(5)	54(3)
C(6)	-693(9)	3239(3)	2470(4)	45(3)	3339(4)	250(4)	3311(4)	45(2)
C(N1)	1453(9)	5571(3)	1432(5)	43(3)	-1290(5)	673(4)	1009(5)	60(3)
C(N2)	4981(9)	5674(3)	2887(5)	45(3)	-1729(4)	2411(4)	2180(4)	60(3)
O(3)	4270(7)	3344(2)	24(3)	56(2)	-	-	-	-
O(4)	-	-	-	-	5076(3)	1227(3)	892(3)	74(2)
C(31)	4550(10)	2725(3)	-778(6)	59(4)	-	-	-	-
C(41)	-	-	-	-	4794(6)	1942(5)	-271(5)	86(4)
3								
	Part A				Part B			
	x/a	y/b	z/c	U_{eq}	x/a	y/b	z/c	U_{eq}
Pd	2680.6(6)	6557.1(3)	199.3(3)	38.0(3)	1315.6(6)	5273.9(3)	1532.0(3)	37.3(3)
Cl	3812(2)	5683(1)	1140(1)	50(1)	224(2)	6268(1)	786(1)	59(1)
N(21)	4818(6)	6868(3)	-314(4)	45(3)	-832(6)	4845(3)	1871(3)	44(3)
C(1)	1799(8)	7226(3)	-614(4)	39(4)	2174(7)	4515(3)	2192(4)	44(4)
C(2)	2911(9)	7442(4)	-1236(5)	53(4)	1062(8)	4000(3)	2336(4)	49(4)
C(21)	4495(8)	7104(4)	-1230(5)	60(5)	-541(8)	4117(3)	1915(5)	55(4)
C(3)	2439(10)	7920(4)	-1842(5)	64(5)	1489(9)	3447(3)	2797(5)	57(4)
C(4)	908(10)	8164(4)	-1863(6)	60(5)	3041(9)	3377(3)	3131(5)	60(4)
C(5)	-207(8)	7933(4)	-1254(5)	52(4)	4100(8)	3879(4)	2990(4)	53(4)
C(6)	245(8)	7471(3)	-640(5)	42(4)	3684(7)	4450(3)	2538(4)	46(4)
C(N1)	5424(10)	7421(4)	223(6)	70(5)	-1284(9)	5099(4)	2748(5)	64(4)
C(N2)	6104(9)	6344(4)	-360(6)	67(5)	-2148(8)	4970(4)	1247(5)	67(5)
O(5)	-1753(6)	8125(3)	-1229(4)	74(4)	5667(6)	3873(3)	3267(4)	74(3)
C(51)	-2352(11)	8549(4)	-1935(6)	88(6)	6255(13)	3320(5)	3784(7)	93(7)
C(1)t	-451(16)	4407(7)	5085(8)	61(3) ^b				
C(2)t	-1578(16)	4995(7)	5039(8)	87(3) ^b				
C(3)t	969(16)	4397(7)	5047(9)	77(3) ^b				
C(11)t ^a	-2981(31)	5077(13)	5013(17)	89(6) ^b				

^a The methyl group of the toluene is disordered over two sites related by $\bar{1}$ and has half the occupancy of the ring carbons. ^b Refined isotropically.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (degrees) FOR 1, 2 AND 3 (Primed atoms are generated by the inversion operation $(-x, -y, -z)$)

	1	2	3	
			A	B
<i>a. Distances</i>				
Pd–Pd	3.535(1)	3.509(1)	3.502(2)	–
Pd–Cl	2.471(1)	2.488(2)	2.467(2)	2.478(2)
Pd–Cl'	2.341(1)	2.334(2)	2.337(2)	2.338(2)
Pd–C(1)	1.976(5)	1.986(3)	1.981(6)	1.967(6)
Pd–N(21)	2.075(4)	2.069(3)	2.068(5)	2.072(5)
C(1)–C(2)	1.388(7)	1.401(6)	1.418(10)	1.412(9)
C(2)–C(3)	1.396(6)	1.399(7)	1.395(11)	1.366(9)
C(2)–C(21)	1.520(7)	1.488(6)	1.494(10)	1.510(9)
C(3)–C(4)	1.373(6)	1.373(6)	1.376(12)	1.406(11)
C(4)–C(5)	1.374(8)	1.394(7)	1.415(11)	1.363(10)
C(5)–C(6)	1.379(7)	1.386(7)	1.380(10)	1.386(10)
C(6)–C(1)	1.400(7)	1.400(6)	1.396(10)	1.379(9)
C(21)–N(21)	1.503(6)	1.510(6)	1.520(9)	1.482(8)
N(21)–C(N1)	1.490(6)	1.479(3)	1.475(10)	1.505(9)
N(21)–C(N2)	1.477(6)	1.496(6)	1.509(10)	1.484(9)
C(3)–O(31)	1.377(6)	–	–	–
O(31)–C(31)	1.429(6)	–	–	–
C(4)–O(41)	–	1.384(6)	–	–
O(41)–C(41)	–	1.437(7)	–	–
C(5)–O(51)	–	–	1.356(9)	1.389(9)
O(51)–C(51)	–	–	1.472(11)	1.450(12)
<i>b. Angles</i>				
Cl–Pd–Cl'	85.5(1)	86.7(1)	86.0(1)	85.7(1)
Cl–Pd–C(1)	178.4(1)	173.9(1)	176.7(2)	176.5(2)
Cl–Pd–N(21)	96.6(1)	95.2(1)	96.4(1)	97.7(1)
C(1)–Pd–N(21)	82.6(2)	82.8(2)	82.6(2)	82.1(2)
C(1)–Pd–Cl'	95.2(1)	95.4(1)	95.1(2)	94.7(2)
N(21)–Pd–Cl'	176.9(1)	178.0(1)	176.8(2)	176.0(2)
Pd–C(1)–C(6)	126.6(4)	127.1(3)	126.9(5)	127.4(5)
Pd–C(1)–C(2)	114.4(3)	113.6(3)	113.3(4)	114.1(4)
Pd–N(21)–C(21)	108.0(3)	108.2(3)	107.8(4)	106.1(4)
Pd–N(21)–C(N1)	107.0(3)	108.0(3)	107.8(4)	108.5(4)
Pd–N(21)–C(N2)	115.1(3)	113.9(3)	115.6(4)	114.2(4)
Pd–Cl–Pd'	94.5(1)	93.3(1)	93.5(1)	93.2(1)
C(2)–C(21)–N(21)	108.4(4)	108.4(3)	107.4(6)	108.6(5)
C(21)–N(21)–C(N1)	109.7(4)	110.1(4)	110.6(6)	109.5(5)
C(21)–N(21)–C(N2)	108.6(4)	108.3(4)	107.1(5)	108.5(5)
C(N1)–N(21)–C(N2)	108.3(4)	108.3(3)	107.9(5)	109.9(5)
C(6)–C(1)–C(2)	119.0(4)	119.1(4)	119.7(6)	118.5(6)
C(1)–C(2)–C(21)	116.4(4)	116.8(4)	116.7(6)	114.0(6)
C(1)–C(2)–C(3)	121.1(4)	121.0(4)	118.9(7)	120.4(6)
C(3)–C(2)–C(21)	122.4(5)	122.2(4)	124.2(7)	125.5(6)
C(2)–C(3)–C(4)	119.2(5)	118.9(4)	121.3(8)	120.8(6)
C(3)–C(4)–C(5)	119.8(5)	121.0(5)	119.5(7)	118.1(6)
C(4)–C(5)–C(6)	122.0(5)	120.4(4)	120.1(7)	122.0(6)
C(5)–C(6)–C(1)	118.9(5)	119.6(4)	120.5(7)	120.1(6)
C(2)–C(3)–O(31)	115.8(4)	–	–	–
C(4)–C(3)–O(31)	125.0(4)	–	–	–
C(3)–O(31)–C(31)	116.9(4)	–	–	–

continued

TABLE 3 (continued)

	1	2	3	
			A	B
C(3)–C(4)–O(41)	–	123.8(4)	–	–
C(5)–C(4)–O(41)	–	115.2(2)	–	–
C(4)–O(41)–C(41)	–	117.1(4)	–	–
C(4)–C(5)–O(51)	–	–	124.5(7)	124.5(7)
C(6)–C(5)–O(51)	–	–	115.4(6)	113.5(6)
C(5)–O(51)–C(51)	–	–	117.6(6)	119.4(6)

are constrained to special positions over inversion centres at 0,0,0 and 1/2,1/2,1/2 in the cell, were refined initially with the methyl carbon at half occupancy. The inference is that this group is disordered over two inversion-related sites. Although the occupancy was consistent with the elemental analysis, the isotropic temperature factors for the atoms of this molecule were abnormally high, and the subsequent refinement of occupancy factors gave values close to 0.5 (0.25 for the methyl carbon). These were used in the final refinement cycles. It is therefore assumed that the lability of the toluene molecules is such that partial solvent loss from the structure occurs without detriment to the lattice stability. This was evident in the constancy of the three standard reflections monitored throughout the data collection period. The residuals are defined as follows: $R = [\sum |F_0| - |F_c|] / \sum |F_0|$ and $R_w = [(\sum w |F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2}$. Hydrogen atoms were located from difference-Fourier syntheses and included in the refinements at fixed positions with their isotropic U values set invariant at 0.05 Å². Neutral atom scattering factors were used [17], corrected where appropriate for anomalous dispersion [17]. Final atomic parameters and equivalent isotropic thermal parameters are given in Table 2, while anisotropic thermal parameters and observed and calculated structure factors are available from the authors. Comparative bond distances and angles are given in Table 3.

Discussion

Isomeric complexes **1**, **2** and **3** are, as pre-empted in the previous report [2], bis-chloro-bridged dimers with the chelate rings *trans*-related (Fig. 1). In both **1** and **2**, the dimers are centrosymmetric, lying on crystallographic inversion centres in their respective unit cells. However, molecules of **3** are situated at general positions in the unit cell and are conformationally different from the *ortho*- and *para*-isomers. A comparison of torsion angles about the chelate rings in all three complexes (Table 4) shows the marked difference particularly in the relative dispositions of the independent chelate rings (**A** and **B**) in complex **3**. This observation is consistent with the failure of **3** (cf. **1** and **2**) to give good crystal morphology when grown from chloroform, since each molecule is unable to occupy inversion centres because of this subtle loss of centrosymmetry. With toluene as a solvent, the crystals form with the complex molecules in general positions aided by the space filling toluene molecules which partially occupy the general cell positions at 0,0,0 and 1/2,1/2,1/2. The dimer molecules have pseudo two-fold rotational symmetry, with a Pd–Pd sep-

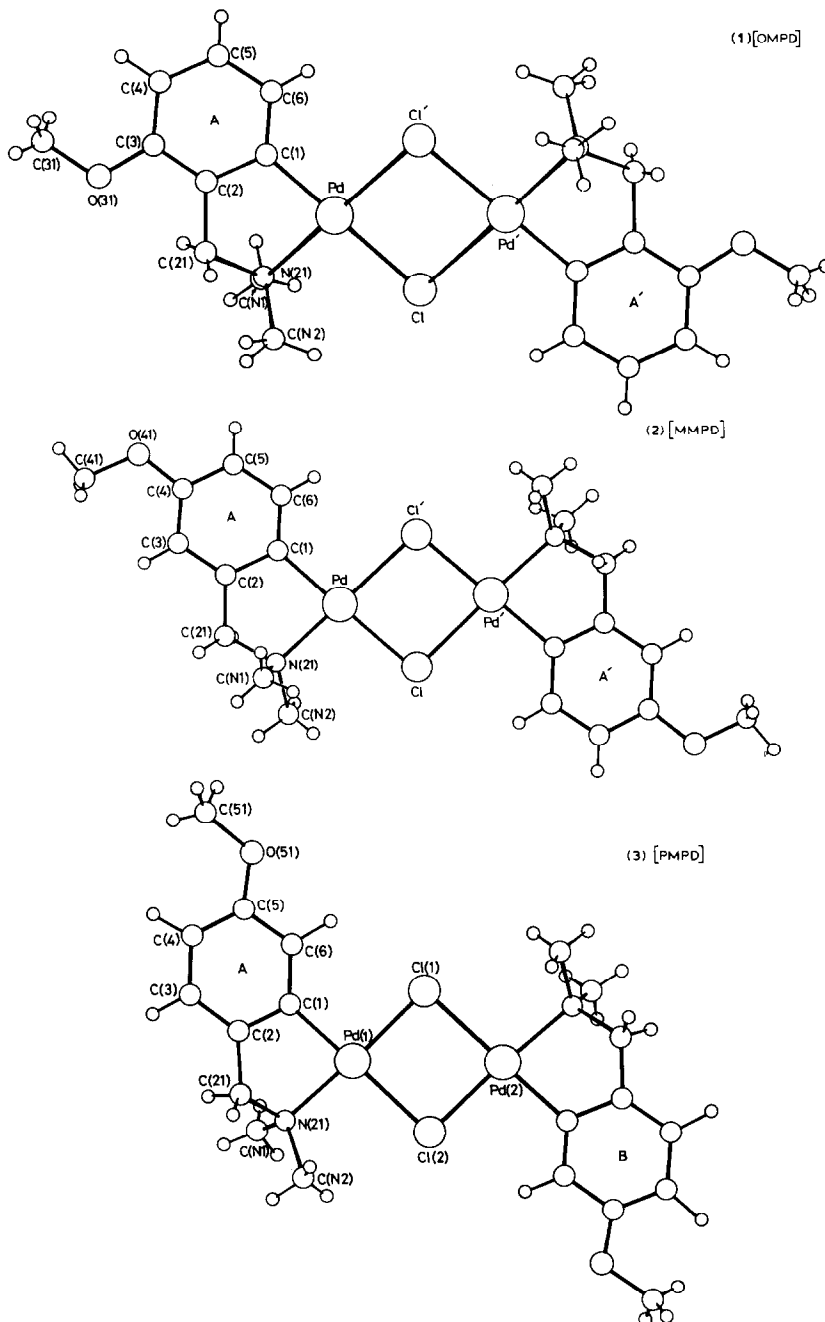


Fig. 1. Molecular conformation and atom naming scheme for complexes 1, 2 and 3. Unless otherwise indicated, atoms are carbons and hydrogens take the number of the parent carbon. For 1 and 2, the primed section of the molecule is generated by crystallographic inversion symmetry while for 3, the B part of the molecule is related to A by pseudo-inversion.

TABLE 4

COMPARATIVE TORSION ANGLES ABOUT THE CHELATE RINGS OF THE DIMERIC COORDINATION POLYHEDRONS IN **1**, **2** AND **3**

	1	2	3	
			A	B
Cl-Pd-C(1)-C(2)	+75.3	-169.0	-58.3	-161.2
Cl'-Pd-C(1)-C(2)	-167.7	+81.6	-168.4	+102.5
Pd-C(1)-C(2)-C(21)	+1.2	+7.4	+4.6	+3.0
C(1)-C(2)-C(21)-N(11)	-23.7	-27.9	-27.9	-30.1
C(2)-C(21)-N(11)-Pd	+33.1	+33.7	+36.6	+40.8
C(2)-C(21)-N(11)-C(N1)	-83.2	-84.2	-81.0	-76.2
C(2)-C(21)-N(11)-C(N2)	+158.5	+157.6	+161.7	+163.9

ation (3.502(1) Å) similar to the distances for **1** (3.535(2) Å) and **2** (3.509(1) Å). There is a significant twist within the five-membered chelate rings of **1** particularly about the substituted nitrogen donor group, resulting in one of the methyl substituents lying almost in the chelate plane with the other perpendicular. By comparison, in **2**, the chelate ring is much less convoluted in this region and the methyl groups are almost mirror related across the chelate plane. In addition, the methoxy group in the phenyl ring is directed away from the substituted nitrogen in **1**, opposite to that found for **2** and **3**, but in all three complexes, the groups are essentially coplanar with the phenyl rings. The opposite conformation in **1** is tenable on the basis of intramolecular repulsions due to the steric effects of the methyl groups.

The coordination about each palladium in all compounds is approximately square planar with the bonds to carbon, nitrogen and the chlorines closely comparable across the series (1.976(5), 2.075(4), 2.341(1), 2.471(1) Å (**1**); 1.986(3), 2.069(3), 2.334(2), 2.488(2) Å (**2**); 1.981(6), 2.068(5), 2.337(2), 2.466(2) Å (**3A**); 1.967(6), 2.072(5), 2.338(2), 2.478(2) Å (**3B**), respectively). These values are also similar to those found for the corresponding distances in complex **4** (1.967(3), 2.027(4), 2.330(1), 2.460(1) Å) [15] despite the presence in this compound of sp^2 bonding to nitrogen in the chelate ring (cf. sp^3 in **1**, **2** and **3**), although as the only consequence the Pd-N bond may be considered shortened (ca. 0.04 Å). Moreover, the Pt^{II} compound in ref. 3 (comparative distances, 1.94, 1.98, 2.33, 2.46 Å), although lacking the high precision of the present analyses, reflects the contention that the Pt^{II} and Pd^{II} compounds are closely similar and that the presence of a substituent such as a methoxy group in the phenyl ring has no significant effect on the strength of the donor carbon or nitrogen to Pd bonds.

The *trans* effect across the complex square plane results in the weakening of the Pd-Cl bond *trans* to the Pd-C(σ) bond (mean, 2.476(2) Å) compared to the one *trans* to the nitrogen (mean 2.337(2) Å). Complex **4** also shows the effect. The comparative distances for the Pt^{II} compound of ref. 3, which are not significantly different from those for **1**, **2** and **3**, indicate that the metal (Pd^{II} or Pt^{II}) is not important in exerting an influence on the magnitude of the *trans* effect. The findings are also consistent with the expected ordering [18] which places C(σ) > N. Differences due to the type of internal bonding i.e. sp^2 or sp^3 involved with the donor

carbon of the ligand do not appear to be significant. For compounds **1** to **4**, the range for equivalent Pd–Cl bonds 2.330–2.338 Å, 2.460–2.488 Å, and the range for the differences (Δl) (0.128–0.154 Å) is small. For the system involving an sp^3 C–Pd σ bond, e.g. di- μ -chlorobis[1-formyl-2,2-dimethyl-3(dimethylamino)propyl-*C,N*]dipalladium(II) [10], the Pd–C bonds and Δl are 2.335, 2.476, 0.141 Å, respectively. In addition the effect of C(σ) vs. C(π) upon the Pd–Cl bond lengths does not appear to be very significant, e.g. di- μ -chlorobis[*endo*-3-phenylnorbornen-2-yl-*endo*]dipalladium(II), respectively 2.40 Å (opposite C(σ)) and 2.40 Å (opposite C(π)) [14].

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