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Cyclopalladated Complexes. Synthesis and Crystal Structure of Di-μ-chloro-bis[(2′,6′-dimethylazobenzenato-C^2,N^2)palladium(II)]

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Abstract. $C_{28}H_{26}Cl_2N_4Pd_2$, M_r = 702·25, monoclinic, $P2_1/n$, a = 12·993 (3), b = 11·739 (3), c = 27·592 (7) Å, β = 99·29 (2)°, V = 4153 (2) Å^3, Z = 6, D_x = 1·69 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 15·0 cm^{-1}, F(000) = 2088, T = 298 K, R = 0·053 and wR = 0·045 for 4341 reflections with $I > 3\sigma(I)$. The complex has a dimeric structure with the 2′,6′-dimethylazobenzene ligands, HL, mutually *trans* with respect to the Pd–Pd axis, and bonded to Pd^{II} atoms which have a square-planar geometry. The two [(L)Pd] moieties are connected by two bridging Cl atoms. The Pd_2Cl_2 core is planar.

Introduction. The bis(chloro)-bridged cyclopalladated compounds are the expected product which forms when species such as azobenzenes are reacted with palladium(II) chloride derivatives (Omae, 1979; Constable, 1984). Nevertheless, in spite of the large number of synthetized complexes, to the best of our knowledge, no X-ray structural data are available for this group of compounds. In this paper we report on the synthesis and crystal structure of the cyclometallated μ-Cl dimer obtained from 2′,6′-dimethylazobenzene.

Experimental. All the starting reagents were used as received without further purification. The 2′,6′-dimethylazobenzene, HL, was prepared by reacting nitrosobenzene (1 mmol) and 2,6-dimethylaniline (1:1 molecular ratio) in acetic acid (6 ml). The mixture was stirred overnight at room temperature; thereafter water (20 ml) and diethyl ether (20 ml) were added. The HL product (red, oily) was separated from the organic layer by chromatography (SiO_2/petroleum ether 313–333 K) and characterized by IR and NMR spectroscopies.

The complex [(L)PdCl]$_2$, was prepared treating an ethanolic solution (10 ml) containing 1 mmol of HL with $(PhCN)_2PdCl_2$ (1:1 molecular ratio). The mixture was stirred at room temperature for 12 h. The orange solid which forms was filtered, washed with pentane and dried under vacuum (yield 70%). Anal. calc. for $C_{28}H_{26}Cl_2N_4Pd_2$: C, 47·89; H, 3·73; N, 7·98. Found: C, 48·03; H, 3·77; N, 8·06.

Crystals suitable for X-ray analysis have been obtained from ethanol. An orange crystal 0·12 × 0·14 × 0·22 mm was used for intensity data collection. X-ray diffraction measurements were performed with a Siemens $R3m/V$ four-circle diffractometer, ω-scan technique, graphite-monochromated Mo $K\alpha$ radiation, scan range 2θ = 1–50° (−1

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*
Pd(1)	8778 (1)	5167 (1)	−357 (1)	45 (1)
Pd(2)	1840 (1)	167 (1)	1989 (1)	50 (1)
Pd(3)	4378 (1)	−33 (1)	1746 (1)	50 (1)
Cl(1)	9523 (2)	4329 (2)	438 (1)	55 (1)
Cl(2)	3502 (2)	512 (2)	2429 (1)	59 (1)
Cl(3)	2728 (2)	−389 (3)	1307 (1)	79 (1)
N(1)	7281 (5)	4823 (6)	−342 (2)	47 (2)
N(2)	6583 (6)	5203 (7)	−680 (3)	62 (3)
N(3)	378 (5)	−218 (6)	1684 (3)	48 (3)
N(4)	−363 (5)	6 (6)	1918 (3)	53 (3)
N(5)	5849 (5)	215 (6)	2073 (2)	49 (3)
N(6)	6596 (5)	10 (6)	1841 (3)	51 (3)
C(1)	8112 (7)	5849 (7)	−978 (3)	49 (3)
C(2)	8538 (7)	6359 (9)	−1343 (4)	64 (4)
C(3)	7904 (9)	6816 (8)	−1757 (4)	69 (4)
C(4)	6845 (9)	6768 (9)	−1797 (4)	79 (5)
C(5)	6397 (8)	6257 (9)	−1439 (4)	77 (4)
C(6)	7029 (7)	5803 (8)	−1034 (3)	54 (4)
C(7)	6896 (6)	4184 (8)	40 (3)	44 (3)
C(8)	6407 (7)	4732 (9)	381 (3)	59 (4)
C(9)	6084 (8)	4092 (12)	748 (4)	78 (5)
C(10)	6242 (9)	2948 (12)	769 (4)	88 (5)
C(11)	6740 (8)	2407 (9)	422 (4)	68 (4)
C(12)	7088 (7)	3036 (8)	62 (3)	52 (4)
C(13)	7633 (8)	2463 (8)	−314 (4)	74 (4)
C(14)	6233 (8)	6010 (10)	367 (4)	88 (5)
C(15)	1060 (6)	720 (7)	2500 (3)	49 (3)
C(16)	−2 (6)	534 (8)	2365 (3)	52 (3)
C(17)	−727 (7)	863 (8)	2664 (4)	63 (4)
C(18)	−346 (8)	1417 (9)	3098 (4)	67 (4)
C(19)	707 (8)	1645 (8)	3228 (3)	70 (4)
C(20)	1409 (7)	1295 (8)	2933 (4)	64 (4)
C(21)	41 (6)	−711 (7)	1207 (3)	44 (3)
C(22)	199 (7)	−1873 (8)	1151 (3)	54 (4)
C(23)	−188 (8)	−2337 (8)	685 (4)	65 (4)
C(24)	−679 (8)	−1658 (10)	320 (4)	68 (4)
C(25)	−783 (8)	−522 (9)	381 (4)	64 (4)
C(26)	−420 (7)	−6 (8)	830 (3)	53 (3)
C(27)	−545 (8)	1241 (9)	893 (3)	78 (5)
C(28)	759 (8)	−2596 (8)	1552 (4)	79 (4)
C(29)	5139 (6)	−447 (7)	1213 (3)	46 (3)
C(30)	6228 (6)	−364 (7)	1364 (3)	47 (3)
C(31)	6939 (7)	−608 (8)	1054 (3)	56 (4)
C(32)	6555 (8)	−978 (8)	576 (4)	63 (4)
C(33)	5493 (8)	−1056 (9)	426 (3)	65 (4)
C(34)	4800 (7)	−800 (9)	737 (3)	67 (4)
C(35)	6187 (6)	653 (9)	2567 (3)	50 (3)
C(36)	6228 (7)	−68 (10)	2959 (4)	66 (4)
C(37)	6578 (9)	392 (13)	3425 (4)	89 (6)
C(38)	6832 (10)	1509 (15)	3466 (4)	95 (6)
C(39)	6771 (8)	2205 (11)	3074 (5)	87 (5)
C(40)	6435 (7)	1806 (10)	2611 (3)	62 (4)
C(41)	6310 (8)	2554 (9)	2172 (4)	88 (5)
C(42)	5914 (9)	−1289 (11)	2894 (4)	98 (6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Molecule *A*			
Pd(1)—Cl(1*a*)	2·330 (2)	Pd(1)—N(1)	1·994 (1)
Pd(1)—Cl(1)	2·456 (2)	N(1)—N(2)	1·272 (9)
Pd(1*a*)—Cl(1)	2·330 (2)	N(2)—C(6)	1·403 (12)
Pd(1*a*)—Cl(1*a*)	2·456 (2)	C(1)—C(6)	1·391 (13)
Pd(1)—C(1)	1·961 (8)		
Molecule *B*			
Pd(2)—Cl(2)	2·335 (2)	Pd(3)—N(5)	1·998 (6)
Pd(2)—Cl(3)	2·451 (3)	N(3)—N(4)	1·271 (10)
Pd(3)—Cl(3)	2·324 (2)	N(5)—N(6)	1·267 (10)
Pd(3)—Cl(2)	2·439 (3)	N(4)—C(16)	1·391 (11)
Pd(2)—C(15)	1·974 (9)	N(6)—C(30)	1·397 (11)
Pd(3)—C(29)	1·962 (9)	C(15)—C(16)	1·387 (11)
Pd(2)—N(3)	2·002 (6)	C(29)—C(30)	1·412 (11)
Molecule *A*			
Pd(1)—Cl(1)—Pd(1*a*)	93·2 (1)	N(1)—Pd(1)—C(1)	78·9 (3)
Cl(1)—Pd(1)—Cl(1*a*)	86·8 (1)	N(2)—N(1)—Pd(1)	119·8 (6)
C(1)—Pd(1)—Cl(1*a*)	96·0 (3)	N(2)—C(6)—C(1)	117·9 (7)
C(1)—Pd(1)—Cl(1)	176·8 (3)	C(6)—N(2)—N(1)	111·1 (7)
N(1)—Pd(1)—Cl(1)	98·3 (2)	C(6)—C(1)—Pd(1)	112·1 (6)
N(1)—Pd(1)—Cl(1*a*)	174·8 (2)		
Molecule *B*			
Pd(2)—Cl(2)—Pd(3)	93·5 (1)	N(5)—Pd(3)—Cl(3)	174·8 (2)
Pd(2)—Cl(3)—Pd(3)	93·5 (1)	N(3)—Pd(2)—C(15)	79·2 (3)
Cl(2)—Pd(2)—Cl(3)	86·3 (1)	N(5)—Pd(3)—C(29)	79·2 (3)
Cl(2)—Pd(3)—Cl(3)	86·8 (1)	N(4)—N(3)—Pd(2)	118·9 (5)
C(15)—Pd(2)—Cl(2)	96·3 (2)	N(6)—N(5)—Pd(3)	119·9 (5)
C(29)—Pd(3)—Cl(3)	95·6 (2)	N(4)—C(16)—C(15)	119·1 (8)
C(15)—Pd(2)—Cl(3)	174·9 (3)	N(6)—C(30)—C(29)	118·3 (8)
C(29)—Pd(3)—Cl(2)	177·6 (2)	C(16)—N(4)—N(3)	111·7 (6)
N(3)—Pd(2)—Cl(3)	98·6 (2)	C(30)—N(6)—N(5)	111·2 (6)
N(5)—Pd(3)—Cl(2)	98·4 (2)	C(16)—C(15)—Pd(2)	111·1 (6)
N(3)—Pd(2)—Cl(2)	173·2 (2)	C(30)—C(29)—Pd(3)	111·3 (6)

$\leq h \leq 14$, $0 \leq k \leq 13$, $-32 \leq l \leq 32$). Accurate unit-cell dimensions were obtained from least-squares refinement of 25 strong reflections in the $14 < 2\theta < 30°$ range. No systematic loss of intensity of three standard reflections ($\bar{4}\bar{3}\bar{1}$, $0\bar{4}3$, $0,\bar{1},\overline{11}$) was observed during data collection. The $P2_1/n$ symmetry was checked by the Le Page method (Spek, 1988). 8789 reflections were measured (7299 unique, $R_{\rm int} = 0·023$), and Lorentz and polarization corrections applied to the intensity data. Empirical correction for the absorption was performed using the ψ-scan method with reflections at χ angles about 90°.

The structure was solved by Patterson and Fourier techniques. 4341 reflections having $I > 3\sigma(I)$ were used to refine 487 parameters by full-matrix least squares (on F) [$\sum w(|F_o| - |F_c|)^2$ minimized]. All non-H atoms were refined anisotropically, while H atoms were positioned in calculated positions, with a common thermal parameter. Final $R = 0·053$, $wR = 0·045$, $w^{-1} = \sigma^2(F) + 0·000102F^2$, $S = 2·01$, largest and average $\Delta/\sigma = 0·22$, 0·002, max. and min. $\Delta\rho$ excursions in Fourier syntheses 0·62 and $-0·70$ e Å^{-3} respectively.

All calculations were performed with *SHELXTL* (Sheldrick, 1989) and *PARST* (Nardelli, 1983) packages. Atomic scattering factors were from the *SHELXTL* program.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and selected bond lengths and angles in Table 2.* The title compound shows Pd_2Cl_2 units with bridging Cl atoms (Fig. 1). Each Pd^{II} atom is also involved in a five-membered chelate ring. The metals exhibit the usual square-planar coordination geometry and the *L* ligands adopt a *trans* arrangement with respect to the Pd–Pd axis.

Two independent molecules are present in the unit cell, one of which (*A*) lies on a crystallographic

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* Lists of structure factors, anisotropic thermal parameters, full bond lengths, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53738 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

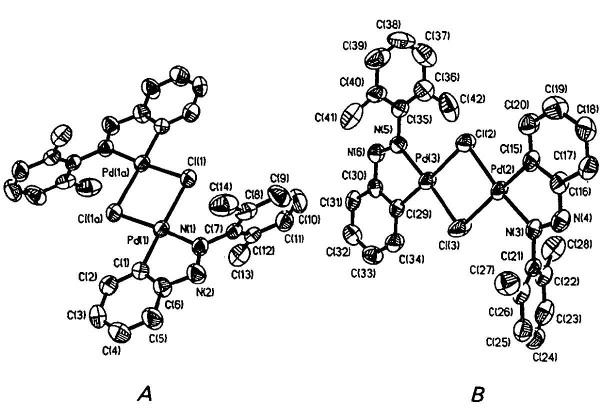

Fig. 1. *ORTEP* (Johnson, 1965) view of the complex $C_{28}H_{26}Cl_2N_4Pd_2$ with molecules *A* and *B*. H atoms are omitted for clarity.

inversion centre. The length of the Pd—Cl bond *trans* to C, and the Pd—Cl bond *trans* to N are in agreement with the stronger *trans* effect exerted by a σ-bonded phenyl ring (Barr, Dyke, Smith, Kennard & McKee, 1985) and within the range expected.

The few X-ray structural analyses carried out on similar cyclopalladated compounds show that in the solid state the Pd_2Cl_2 fragment can be either planar (Barr, Dyke, Smith, Kennard & McKee, 1985) or bent, with a dihedral angle between $PdCl_2$ planes of 58° (Constable, McDonald, Sawkins & Shaw, 1980) or 39° (Ghedini, Armentano, De Munno, Crispini & Neve, 1990). In the present case, the Pd_2Cl_2 fragment is strictly planar in molecule *A* and nearly planar in molecule *B*.

Some distortions can be observed in one molecule with respect to the other. In fact, with respect to the Pd_2Cl_2 plane the five-membered metallocycles form a dihedral angle of 3·1 (2)° in *A* and of 7·3 (2), 0·7 (2)° in *B*. The planes of the dimethyl-substituted phenyl groups form, with the metallocycle planes, dihedral angles of 72·9 (3), 72·9 (3), 75·3 (2) and 100·1 (3)°. Therefore the methyl groups are on opposite sides of the Pd_2Cl_2 planes. The shortest Pd–C distances, namely Pd(1)–C(13), Pd(1*a*)–C(13*a*), Pd(2)–C(28) and Pd(3)–C(42), are 3·52 (1), 3·52 (1), 3·66 (1) and 3·76 (1) Å, respectively. Therefore the methyl groups, through an H atom, might be thought as interacting with the metal in a pseudo-axial position.

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Structure of Tris(η^5-cyclopentadienyl)yttrium(III)*

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Abstract. $[Y(C_5H_5)_3]$, $M_r = 284{\cdot}2$, orthorhombic, $P2_1cn$ (non-standard setting of $Pna2_1$), $a = 8{\cdot}631$ (3), $b = 13{\cdot}910$ (4), $c = 19{\cdot}662$ (4) Å, $V = 2360$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}599$ g cm^{-3}, λ(Mo $K\alpha$) = 0·709261 Å, $\mu = 48{\cdot}3$ cm^{-1}, $F(000) = 1152$, $T = 295$ K, $R = 0{\cdot}059$ for 1558 reflections [$I > 1{\cdot}5\sigma(I)$]. Each Y atom is η^5-bonded to three cyclopentadienyl rings, individual $[Y(C_5H_5)_3]$ molecules being loosely aligned to form zigzag chains as in the lanthanoid homologues $[Ln(C_5H_5)_3]$ with Ln = Er and Tm. The structure of

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[*] Coordination Behaviour in Base-Free Tris(cyclopentadienyl) Complexes of Rare Earth Elements. VII. Part VI: Paolucci, Fischer, Breitbach, Pelli & Traldi (1988).

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