Journal of Organometallic Chemistry, 427 (1992) 409–414
Elsevier Sequoia S.A., Lausanne
JOM 22433

Cyclopalladated complexes. Synthesis and crystal structure of di-μ-chloro-bis{[2,6-dimethyl-N-(benzylidene)phenylaminato-$C^{2\prime}$,N]palladium(II)}

Alessandra Crispini, Giovanni De Munno, Mauro Ghedini and Francesco Neve
Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS) (Italy)

(Received July 12, 1991)

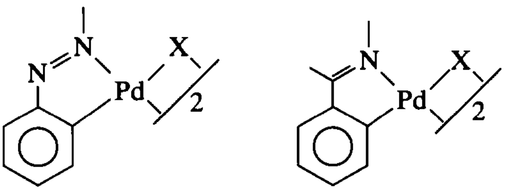
Abstract

The X-ray crystal structure of the cyclometallated palladium(II) complex [{Pd(L2)(μ-Cl)}$_2$], L2 = 2,6-dimethyl-N-(benzylidene)phenylaminate, is described. Crystals were orthorhombic, space group $Pna2_1$ with $a = 17.307(3)$ Å, $b = 17.732(4)$ Å, $c = 9.075(2)$ Å, $Z = 4$, $U = 2785.0(10)$ Å^3.

The palladated dimer, with asymmetrically bridging chlorine atoms, exhibits a Pd_2Cl_2 unit folded at 36.7(1)° and a non-bonding Pd $\cdots$ Pd separation of 3.425(1) Å.

Introduction

Azobenzenes and aromatic imines are both substrates prone to metallation by appropriate palladium(II) compounds. The usual products are cyclopalladated dimers of general formula [{Pd(L)(μ-X)}$_2$], where X = halide or OAc, whose molecular structures have not been extensively investigated [1–4]. Consequently, the particular structural features of the pertinent cyclometallated rings in I and II are not yet well known.



(I) (II)

Scheme 1

Correspondence to: Professor M. Ghedini, Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy.

In a previous paper [5] we reported the X-ray analysis of the complex $[\{Pd(L1)(\mu\text{-}Cl)\}_2]$ where L1 is 2′,6′-dimethylazobenzenate (palladacycle I). For comparison, it is worth considering the homologous organometallic compounds with the palladacycle II obtained from 2,6-dimethyl-*N*-(benzylidene)aniline, HL2. Here we describe the single crystal X-ray structure of the complex $[\{Pd(L2)(\mu\text{-}Cl)\}_2]$.

Experimental

The compound 2,6-dimethyl-*N*-(benzylidene)aniline (HL2) was obtained as a yellow viscous liquid by reaction of benzaldehyde (1 ml, 9.84 mmol) and 2,6-dimethylaniline (1.21 ml, 9.84 mmol) in ethanol (10 ml) under reflux (2 h). Yield 87%. IR (neat): ν(C=N) 1622 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.19 (s, –C(H)=N–), 2.14 (s, CH_3).

A sample of the palladium complex $[\{Pd(L2)(\mu\text{-}Cl)\}_2]$ was synthesized by reaction of $[Pd(PhCN)_2Cl_2]$ (1.43 mmol) and HL2 (1.43 mmol) in ethanol (30 ml) at room temperature (3 h). Yield 90%; m.p. 220°C (dec.). IR (KBr disc): ν(C=N) 1600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2H, –C(H)=N–), 7.28–7.07 (m, 14H; aromatic protons), 2.38 (br s, 12H, CH_3).

Yellow crystals suitable for single-crystal X-ray analysis were obtained from ethanol. The diffraction data were collected on a Siemens R3m/V four-circle diffractometer using graphitemonochromated Mo-K_α radiation. The structure was solved by Patterson methods and completed by Fourier recycling. The test of the *R*-factor ratio (Hamilton) [6] was performed to determine the absolute structure. The result of this clearly indicated the original choice to be correct.

324 parameters were refined by a full-matrix least-squares procedure minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w^{-1} = \sigma^2|F_o| + q|F_c|^2$, with $q = 0.0003$. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned in calculated positions with common thermal parameters ($U = 0.008$ Å^2). The methyl hydrogen atoms were located towards the end of refinement and set at fixed positions. All calculations were performed with SHELXTL PLUS [7] and PARST [8] programs. Atomic scattering factors were as implemented in the SHELXTL PLUS program.

Crystallographic data are reported in Table 1. A complete table of bond lengths and angles and lists of positional parameters of H atoms, structure factors and thermal parameters are available from the authors.

Results and discussion

Selected bond lengths and angles are listed in Table 2 and final atomic coordinates and equivalent isotropic temperature factors in Table 3. The molecular structure and its numbering scheme are shown in Fig. 1.

In the complex each L2 ligand is bonded to the di-μ-chloro-bridge unit through nitrogen atom and an aromatic carbon atom providing two equivalent five-membered $\overline{N–C–Pd–C–C}$ chelate rings. The palladium atoms adopt the expected square planar coordination geometry with the two cyclometallated ligands in a *trans* arrangement with respect to the Pd···Pd axis. The Pd_2Cl_2 rhombus deviates significantly from planarity [the maximum deviation from the plane of the other atoms of the ring being 0.389(2) Å at Cl(2)] and has considerable folding,

Table 1

Crystal data, data collection and structure solution parameters

Formula	$C_{30}H_{28}N_2Cl_2Pd_2$
Molecular wt	700.2
Crystal size (mm)	0.40 × 0.20 × 0.30
Space group	$Pna2_1$
Temperature (K)	298
Cell dimensions:	
a (Å)	17.307(3)
b (Å)	17.732(4)
c (Å)	9.075(2)
U (Å^3)	2785.0(10)
Z	4
$D_{calc.}$ (g/cm^3)	1.67
$F(000)$	1392
Radiation (Å)	Mo-K_{α}, 0.71069
Scan range (deg)	$3 < 2\theta < 54$
Scan method	$\omega - 2\theta$
Independent reflections	3252
Observed reflections	2684 ($I > 3\sigma(I)$)
μ(Mo-K_{α}) (cm^{-1})	14.90
R [a]	0.0300
R_w [b]	0.0301
Goodness of fit [c]	1.42

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. [c] $\mathrm{GOF} = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

with a dihedral angle of 36.7(1)° between the two $PdCl_2$ fragments. The Pd ··· Pd distance [3.425(1) Å] excludes the possibility of a metal–metal bond. The lengths of the Pd–Cl bonds *trans* to C [2.467(2), 2.452(2) Å], and the Pd–Cl bonds *trans* to N

Table 2

Selected bond lengths (Å) and angles (°)

Pd(1)–Cl(1)	2.339(2)	Pd(2)–Cl(1)	2.452(2)
Pd(1)–Cl(2)	2.467(2)	Pd(2)–Cl(2)	2.331(2)
Pd(1)–N(1)	2.054(6)	Pd(2)–N(2)	2.034(6)
Pd(1)–C(1)	1.955(8)	Pd(2)–C(16)	1.970(7)
C(1)–C(2)	1.383(11)	C(16)–C(17)	1.403(11)
C(2)–C(7)	1.454(11)	C(17)–C(22)	1.459(10)
N(1)–C(7)	1.265(10)	N(2)–C(22)	1.257(10)
Pd(1) ··· Pd(2)	3.425(1)		
Cl(1)–Pd(1)–Cl(2)	85.3(1)	Cl(1)–Pd(2)–Cl(2)	85.8(1)
Cl(1)–Pd(1)–C(1)	95.1(2)	Cl(2)–Pd(2)–C(16)	95.2(2)
Cl(2)–Pd(1)–N(1)	98.9(2)	Cl(1)–Pd(2)–N(2)	98.1(2)
N(1)–Pd(1)–C(1)	80.6(3)	N(2)–Pd(2)–C(16)	80.9(3)
Cl(1)–Pd(1)–N(1)	175.5(2)	Cl(2)–Pd(2)–N(2)	176.1(2)
Cl(2)–Pd(1)–C(1)	174.9(2)	Cl(1)–Pd(2)–C(16)	178.0(2)
Pd(1)–C(1)–C(2)	114.0(5)	Pd(2)–C(16)–C(17)	113.4(5)
Pd(1)–N(1)–C(7)	114.4(5)	Pd(2)–N(2)–C(22)	114.9(5)
N(1)–C(7)–C(2)	116.3(7)	N(2)–C(22)–C(17)	117.3(7)
C(1)–C(2)–C(7)	114.5(7)	C(16)–C(17)–C(22)	113.4(7)

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Pd(1)	5959(1)	3753(1)	0	37(1)
Pd(2)	7011(1)	2917(1)	2747(1)	36(1)
Cl(1)	7098(1)	4064(1)	1246(3)	45(1)
Cl(2)	6192(1)	2463(1)	911(3)	53(1)
N(1)	4937(3)	3568(3)	−1094(7)	39(2)
N(2)	7716(3)	3246(3)	4420(7)	41(2)
C(1)	5715(4)	4789(4)	−571(8)	44(2)
C(2)	5011(4)	4867(4)	−1278(9)	43(2)
C(3)	4702(5)	5573(5)	−1655(11)	58(3)
C(4)	5110(6)	6219(5)	−1364(13)	64(3)
C(5)	5840(5)	6146(5)	−727(13)	66(3)
C(6)	6143(4)	5453(4)	−336(10)	53(3)
C(7)	4606(4)	4162(4)	−1543(9)	44(2)
C(8)	4588(4)	2847(4)	−1304(8)	41(2)
C(9)	4940(4)	2337(4)	−2273(11)	52(2)
C(10)	4618(6)	1638(5)	−2444(13)	71(4)
C(11)	3961(7)	1435(6)	−1672(15)	80(4)
C(12)	3601(6)	1944(6)	−770(12)	73(4)
C(13)	3903(4)	2659(5)	−557(9)	54(3)
C(14)	3505(5)	3214(6)	477(12)	73(4)
C(15)	5643(6)	2563(6)	−3110(13)	79(4)
C(16)	6926(4)	2018(4)	4010(9)	41(2)
C(17)	7350(4)	2074(4)	5323(9)	45(2)
C(18)	7346(5)	1509(5)	6400(11)	57(3)
C(19)	6902(5)	872(5)	6138(12)	64(3)
C(20)	6494(5)	792(4)	4861(13)	61(3)
C(21)	6502(5)	1363(4)	3800(10)	51(3)
C(22)	7784(4)	2776(4)	5449(9)	46(2)
C(23)	8124(5)	3967(4)	4524(9)	46(2)
C(24)	8836(4)	4044(5)	3872(10)	50(3)
C(25)	9216(5)	4730(6)	3980(13)	67(4)
C(26)	8882(7)	5307(5)	4765(16)	81(4)
C(27)	8177(6)	5234(5)	5404(12)	71(4)
C(28)	7757(5)	4558(4)	5318(10)	52(3)
C(29)	7012(6)	4447(6)	6028(15)	83(4)
C(30)	9227(5)	3420(6)	3074(13)	76(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

[2.339(2), 2.331(2) Å], parallel the different *trans* influences exerted by the phenyl carbon and the nitrogen atoms [9]. The five-membered chelate rings are essentially planar [0.038(7) Å maximum deviation at C(1) and −0.012(7) Å at C(17)]. Bite angle values [C(1)–Pd(1)–N(1) = 80.6(3)° and C(16)–Pd(2)–N(2) = 80.9(3)°] are in good agreement with those found in structurally related μ-Cl dimers [10–12]. Moreover, with respect to the mean Pd_2Cl_2 plane, the five-membered metallacycles have dihedral angles of 18.5(2) and 15.2(1)°.

The two dimethyl-substituted phenyl groups are planar and nearly orthogonal with respect to the Pd(1) and Pd(2) metallacycle planes, the dihedral angles being 69.2(2) and 94.8(2)°, respectively. As a result, the methyl groups are located above or below the Pd_2Cl_2 fragment with the shortest contact, namely Pd(1) ··· C(15), at 3.57(1) Å.

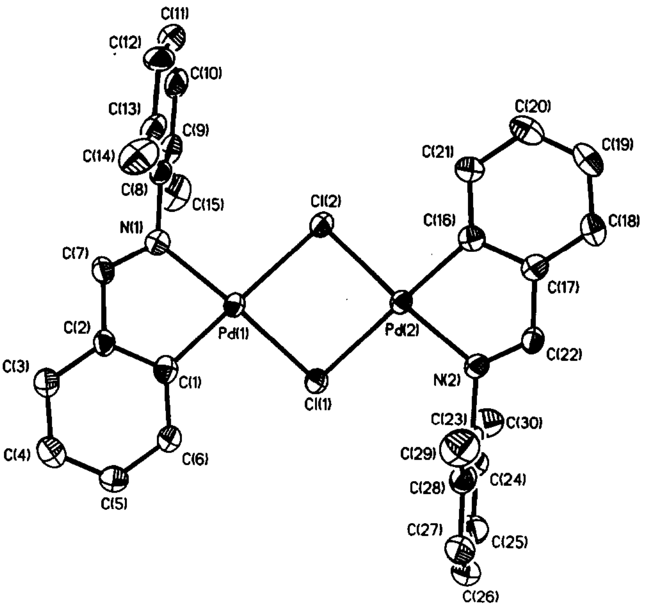


Fig. 1. The molecular structure of [{Pd(L2)(μ-Cl)}$_2$] showing the number scheme adopted. Hydrogen atoms have been omitted for clarity.

Since the molecular structure of [{Pd(L1)(μ-Cl)}$_2$] has been already reported [5], a comparison between that study and the present X-ray analysis is appropriate. The two molecules have similar structural features, the only noticeable difference being the geometry of the Pd_2Cl_2 core, which is strictly planar in [{Pd(L1)(μ-Cl)}$_2$]). As a consequence of the planarity, the two dihedral angles formed between the five-membered metallacycles and the Pd_2Cl_2 plane [*i.e.* 7.3(2) and 0.7(2)°] are smaller than those found in [{Pd(L2)(μ-Cl)}$_2$]). Furthermore, the dimethyl-substituted phenyl groups span larger tilt angles with respect to the Pd(1) or Pd(2) metallacycle planes [75.3(2) and 100.1(3)°] giving rise to the shortest Pd $\cdots$ C(methyl) contacts of 3.66(1) and 3.76(1) Å, respectively.

On the basis of the present data, the metallacycles I and II are extremely similar, the observed folding of the Pd_2Cl_2 group in [{Pd(L2)(μ-Cl)}$_2$] probably being attributable to different solid state effects rather than to different chemistry of L1 and L2.

Acknowledgments

This work was supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R.) and Ministero dell'Università e della Ricerca Scientifica e Tecnologica. We thank Johnson Matthey Research Centre, England, for a generous loan of $PdCl_2$.

References

1 A. Albinati, P.S. Pregosin and R. Rüedi, Helv. Chim. Acta, 68 (1985) 2046.
2 M. Gayoso, M. Alonso, J.M. Vila, E.B. Rivero, W. Hiller and J. Strähle, Acta Crystallogr., Sect. C, 44 (1988) 929.

3 M. Ghedini, S. Armentano, G. De Munno, A. Crispini and F. Neve, Liq. Cryst., 8 (1990) 739.

4 J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernandez and M. Thornton-Pett, J. Organomet. Chem., 401 (1991) 385.

5 S. Armentano, A. Crispini, G. De Munno, M. Ghedini and F. Neve, Acta Crystallogr., Sect. C, 47 (1991) 966.

6 W.C. Hamilton, Acta Crystallogr., 18 (1965) 502.

7 SHELXTL PLUS Version 4.11 (1990), Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA.

8 M. Nardelli, Comput. Chem., 7 (1983) 95.

9 N. Barr, S.F. Dike, G. Smith, C.H.L. Kennard and V. Mc Kee, J. Organomet. Chem., 288 (1985) 109.

10 P.W. Clark, S.F. Dyke and G. Smith, Acta Crystallogr., Sect. C, 41 (1985) 1742.

11 A.A. Watson, D.A. House and P.J. Steel, J. Organomet Chem., 311 (1986) 387.

12 J.W. Suggs and Keu S. Lee, J. Organomet Chem., 299 (1986) 297.