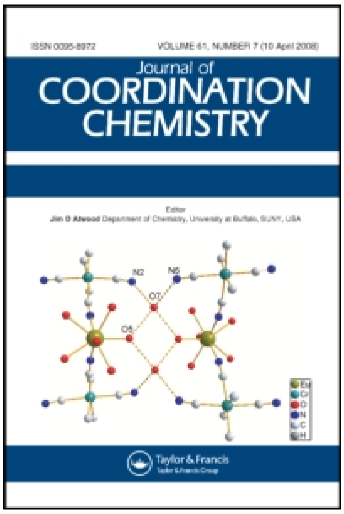

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Synthesis, structure and spectroscopic characterization of 1,2-bis-(2,4,6-trimethylbenzylideneamino) ethanedichloropalladium(II)

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The structure of 1,2-bis(2,4,6-trimethylbenzylideneamino)ethanedichloropalladium(II) was determined by X-ray diffraction methods. The structure derived from NMR and IR spectra and elemental analysis is consistent with it. The complex is orthorhombic, space group *Pcab*, with $a = 14.8662(12)$, $b = 15.0861(13)$, $c = 20.6255(14)$ Å, $V = 4625.7(6)$ Å^3 and $Z = 8$. In the lattice, there exists a weak C–H $\cdots$ Cl hydrogen bond.

Keywords: Palladium(II); 2,4,6-Trimethylbenzylideneamine; Chloride; X-ray structure; Spectroscopy

1. Introduction

Transition metal catalysts have played and will continue to play crucial roles in the synthesis of polymers [1]. Whereas early transition metal catalysts such as Ziegler–Natta and single-side metallocene catalysts [2] remain as workhorses in olefin polymerization, significant advances have been made recently in late transition metal polymerization catalysts [3, 4]. Exciting examples are the nickel(II)- and palladium(II)-α-bis(imine) complexes reported by Brookhart and co-workers [3, 5, 6]. These catalysts show activities comparable to those of the early metal catalysts in polymerizing ethene [7]. On this basis, we thought that Pd–diimine complexes might possibly mediate Heck and Suziki reactions [8–10]. We now report the straightforward preparation of 1,2-bis(2,4,6-trimethylbenzylideneamino)ethanedichloropalladium(II)

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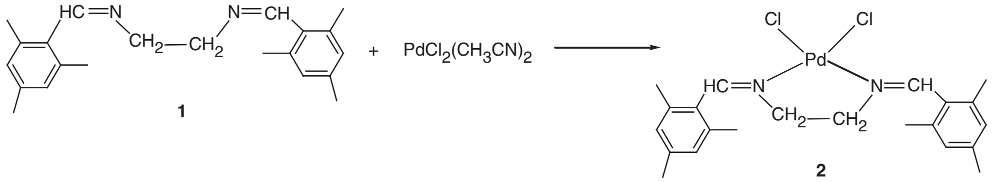

Figure 1. Constitution of the title complex.

and its structural and spectroscopic characterization. The complex was prepared by the reaction shown in figure 1.

2. Experimental

Manipulations were effected using standard Schlenk techniques under dinitrogen with previously dried solvents. 1,2-Bis(2,4,6-trimethylbenzylideneamino)ethane (**1**), was prepared according to known methods [10]. Infrared spectra were recorded (KBr pellets) in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK analysis centre.

2.1. *1,2-Bis(2,4,6-trimethylbenzylideneamino)ethanedichloropalladium(II) (2)*

A solution of 1,2-bis(2,4,6-trimethylbenzylideneamino)ethane (**1**), (0.5 g, 1.55 mmol) in toluene (20 cm^3) and $PdCl_2(CH_3CN)_2$ (0.4 g, 1.55 mmol) were heated for 2 h under reflux. Upon cooling to room temperature, the yellow crystals that had formed were filtered off, washed with Et_2O and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O at room temperature. Yield 0.69 g (89%); melting point: 270°C. Anal. Calcd for $C_{22}H_{28}N_2Cl_2Pd$ (%): C, 53.08; H, 5.67; N, 5.63. Found: C, 53.05; H, 5.70; N, 5.61. IR: $\nu_{(C=N)}$: 1633 cm^{-1}. ^{1}H NMR($CDCl_3$): $\delta = 9.30$ ppm (s, 2H, $N{=}C\mathit{H}C_6H_2(CH_3)_3$-2,4,6); 6.86 (s, 4H, $N{=}CHC_6\mathit{H}_2(CH_3)_3$-2,4,6); 3.25 (s, 4H, $NC\mathit{H}_2C\mathit{H}_2N$); 2.14 and 2.24 (s, 18H, $N{=}CHC_6H_2(C\mathit{H}_3)_3$-2,4,6). ^{13}C-NMR($CDCl_3$): $\delta = 176.2$ ($N{=}\mathit{C}HC_6H_2(CH_3)_3$-2,4,6); 141.2, 134.6, 129.3 and 128.9 ($N{=}CH\mathit{C}_6H_2(CH_3)_3$-2,4,6); 56.7 ($N\mathit{C}H_2\mathit{C}H_2N$); 21.6 and 20.0 ($N{=}CHC_6H_2(\mathit{C}H_3)_3$-2,4,6).

2.2. *Crystallography*

Intensity data were collected at room temperature using an Enraf-Nonius CAD 4 diffractometer [11] with Mo-Kα radiation and using the $\omega/2\theta$ scan mode. Cell parameters were determined from least-squares analysis using 25 centred reflections in the range $2.16° \leq \theta \leq 25.74°$. Three standard reflections measured every 120 min during data collection showed no significant intensity variation. The structure was solved by direct methods using SHELXS-97 [12] in the WinGX package [13] and refined using SHELXL-97 [12]. All non-hydrogen atoms were refined, first with isotropic and then with anisotropic thermal displacement parameters, by full-matrix

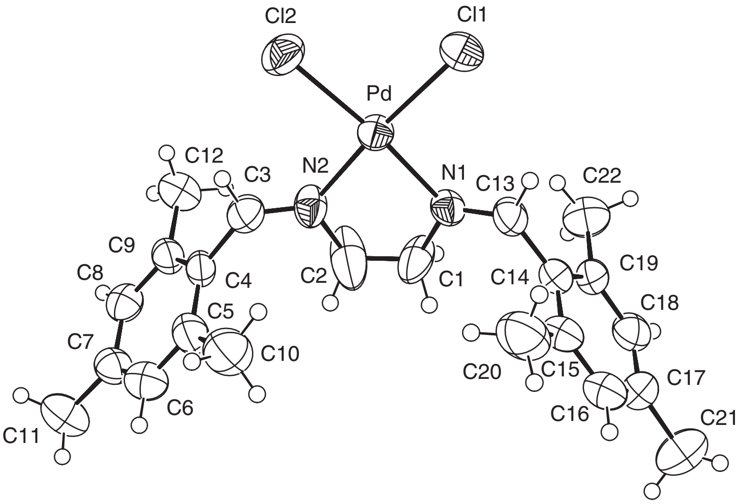

Figure 2. ORTEP drawing of the complex with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

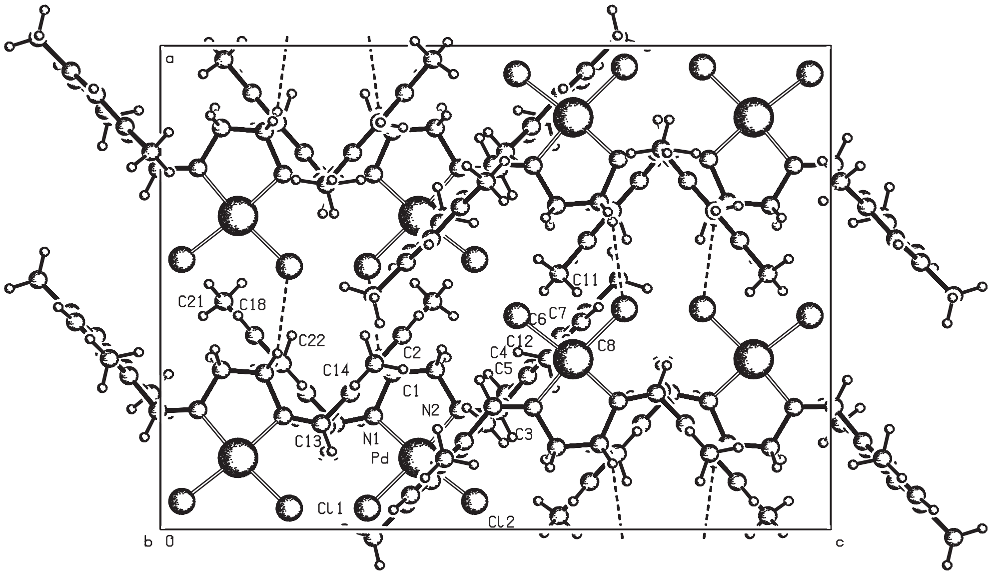

Figure 3. PLATON drawing of hydrogen bonds in the lattice.

least-squares techniques. All hydrogen atoms were placed geometrically and refined as riding with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. An ORTEP drawing [14] of the molecule with 50% probability displacement thermal ellipsoids and the atom numbering scheme is shown in figure 2. A PLATON drawing [15] of hydrogen bonding geometry is shown in figure 3. Crystal and experimental data are given in table 1 and final atomic parameters in table 2. Selected bond lengths and angles are given in table 3.

Table 1. Crystal and experimental data for the structure determination.

Chemical formula	$C_{22}H_{28}Cl_2N_2Pd$
Formula weight	497.76
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pcab*
Unit cell dimensions (Å)	
a	14.8662(12)
b	15.0861(13)
c	20.6255(14)
Volume (Å^3)	4625.7(6)
Z	8
Calculated density (g cm^{-3})	1.429
Absorption coefficient (mm^{-1})	1.042
$F(000)$	2032
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.15$
θ_{max} (°)	25.74
Index range	$-18 \leq h \leq 4$, $0 \leq k \leq 18$, $-24 \leq l \leq 0$
Number of reflections used	4001 ($I \geq 2\sigma(I)$)
Number of parameters	245
R_{int}	0.053
R	0.0415
R_w	0.0855
Goodness-of-fit	0.93
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.403, 0.502

3. Results and discussion

Transition metal complexes based on imine ligands have long been the subject of considerable interest [10]. In the structure of 1,2-bis(2,4,6-trimethylbenzylideneamino) ethanedichloropalladium(II), the palladium is coordinated to two N atoms [Pd–N1 2.034(4) and Pd–N2 2.012(4) Å] of the diimine and two Cl ions [Pd–Cl1 2.2949(13) and Pd–Cl2 2.2948(13) Å]. The Pd–Cl distance is shorter than the Pd–I distance [2.5947(4) Å] of the similar Pd–carbene complex [15]. Coordination geometry around Pd is distorted square planar. Pd is located 0.0104(5) Å above the plane involving N1, N2, Cl1 and Cl2. The dihedral angle between the N1/Pd/N2 and Cl1/Pd/Cl2 moieties is 2.29(13)° and the dihedral angle between the N/Pd/Cl planes is 2.17(11)°. The molecule involves two trimethylbenzyl groups in the asymmetric unit. Two phenyl rings containing atoms B C4–C9 (A) and C14–C19 (B) ring are almost planar. The C8 atom of the A ring and the C14 atom of the B ring have maximum deviations of 0.0133(5) and 0.0141(5) Å from the plane defined by the six atoms of the rings, respectively. Bond distances and angles between the methyl group and phenyl ring are similar for both rings. The methyl C12 atom of the A ring and the C21 atom of the B ring have maximum deviations of 0.0690(6) and 0.0643(8) Å from the phenyl ring planes. The dihedral angle between the phenyl rings is 85.52(14)°. In the Pd/N1/C1/C2/N2 chelate ring (C) the C2 atom has the greatest deviation, 0.209(1) Å, from the plane. Molecules in the lattice are connected by van der Waals interactions. There is one intermolecular hydrogen bond in the crystal between the imidazole ring and a Cl ion with a D $\cdots$ A distance of 3.587(3) Å and a D–H $\cdots$ A angle of 143.0(1)°. Hydrogen bonding is illustrated in figure 3.

Table 2. Final atomic coordinates and equivalent anisotropic thermal parameters for non-hydrogen atoms.

	x/a	y/b	z/c	U_{eq}^*
Pd	0.64803(3)	0.27980(3)	0.384724(19)	0.04718(16)
Cl1	0.54401(10)	0.23830(11)	0.30829(8)	0.0739(5)
Cl2	0.55801(10)	0.23319(11)	0.46848(7)	0.0698(5)
N1	0.7346(3)	0.3286(3)	0.3175(2)	0.0479(11)
N2	0.7474(3)	0.3179(3)	0.4446(2)	0.0543(12)
C1	0.8230(4)	0.3420(6)	0.3455(3)	0.094(3)
C2	0.8299(4)	0.3351(8)	0.4096(3)	0.134(4)
C3	0.7456(4)	0.3330(4)	0.5043(3)	0.0586(15)
C4	0.8179(3)	0.3656(4)	0.5475(2)	0.0496(14)
C5	0.8333(4)	0.4588(4)	0.5533(3)	0.0624(16)
C6	0.8992(4)	0.4861(4)	0.5964(3)	0.0703(18)
C7	0.9478(4)	0.4275(4)	0.6339(3)	0.0584(15)
C8	0.9289(4)	0.3368(4)	0.6273(2)	0.0566(15)
C9	0.8665(4)	0.3063(4)	0.5838(3)	0.0524(14)
C10	0.7806(4)	0.5257(4)	0.5146(3)	0.087(2)
C11	1.0165(4)	0.4588(4)	0.6831(3)	0.087(2)
C12	0.8534(4)	0.2052(4)	0.5767(3)	0.0722(17)
C13	0.7187(3)	0.3554(4)	0.2608(3)	0.0585(16)
C14	0.7814(4)	0.4007(4)	0.2174(3)	0.0527(14)
C15	0.7790(4)	0.4933(4)	0.2138(3)	0.0658(17)
C16	0.8412(5)	0.5348(5)	0.1737(3)	0.087(2)
C17	0.9025(5)	0.4899(6)	0.1362(3)	0.087(2)
C18	0.9013(4)	0.3969(5)	0.1400(3)	0.0701(18)
C19	0.8418(4)	0.3527(4)	0.1789(2)	0.0575(15)
C20	0.7132(5)	0.5467(4)	0.2531(3)	0.096(2)
C21	0.9715(6)	0.5367(6)	0.0942(3)	0.147(4)
C22	0.8428(4)	0.2512(4)	0.1810(3)	0.0742(18)

$^*U_{eq} = (\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \boldsymbol{a_i} \cdot \boldsymbol{a_j}$.

Table 3. Selected bond lengths (Å) and bond angles (°) for the complex.

Pd–N1	2.030(4)	C1–N1	1.450(6)
Pd–N2	2.011(4)	C2–N2	1.447(7)
Pd–Cl1	2.2953(15)	C3–N2	1.251(6)
Pd–Cl2	2.2956(14)	C13–N1	1.259(6)
Cl1–Pd–Cl2	92.33(6)	C3–N2–C2	118.5(5)
N2–Pd–N1	81.38(17)	C3–N2–Pd	129.8(4)
N2–Pd–Cl1	174.52(13)	C2–N2–Pd	111.5(4)
N1–Pd–Cl1	93.26(12)	C2–C1–N1	117.0(5)
N2–Pd–Cl2	93.07(13)	N2–C3–C4	129.6(5)
N1–Pd–Cl2	174.10(12)	N1–C13–C14	126.8(5)
C13–N1–Pd	129.1(4)	C13–N1–C1	119.7(5)
C1–N1–Pd	110.7(3)		

The reaction of 1,2-bis(2,4,6-trimethylbenzylideneamino)ethane (**1**), with $PdCl_2(CH_3CN)_2$ proceeded smoothly in toluene to give complex **2**. The complex is very stable in the solid state. It exhibits a characteristic $\nu_{(C=N)}$ band at 1633. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal imine $(N{=}CHC_6H_2(CH_3)_3\text{-}2,4,6)$ complexes, show that C_{imine} is substantially deshielded; $\delta(^{13}C_{imine})$ is 176.2 ppm. These spectroscopic data are entirely consistent with the results of the crystal structure analysis.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278171. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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