Polyhedron 27 (2008) 3607–3610

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Preparation and crystal structure of binuclear chloro{6-[[chloro-(triphenylphosphine)platinum](mesitylimino)methyl]pyridin-2-yl}bis(triphenylphosphine)platinum(II)

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ARTICLE INFO

Article history:
Received 15 January 2008
Accepted 8 September 2008
Available online 3 November 2008

Keywords:
Binuclear platinum complex
Platinalactam
Centrosymmetric dimer
Imidoyl chlorides

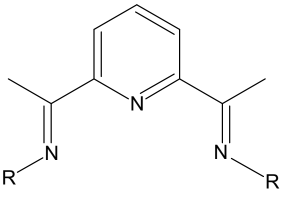
ABSTRACT

Treatment of *N*,*N*′-bis(mesityl)pyridine-2,6-carboxyimidoyl dichloride, **1**, in toluene solution with $[Pt(PPh_3)_4]$ at 100 °C afforded a novel platinacyclic compound, **3**, in 63% yield, instead of the expected compound **2**. The molecular and crystal structures of the title compound, **3**, have been determined by the single crystal X-ray diffraction technique. The coordination geometries around the Pt atoms are distorted square-planar. In the crystal structure, the molecules are linked by a pair of C–H···N hydrogen bonds into a centrosymmetric dimer with an $R_2^2(16)$ ring, centred at (1/2,1/2,1/2).

1. Introduction

Heterocyclic ligands containing nitrogen atoms are drawing a great deal of attention in coordination chemistry and homogeneous catalysis [1–3] because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate ring substituents [4]. Recently, planar tridentate pyridine-bridged *N*,*N*,*N* ligands, such as Pydims (**A**) [5,6] and pyridine-2,6-dicarboxyimidoyl dichloride (**B**) have been synthesized and their reactions have been studied [7].

Reactions of imidoyl chlorides with low valent transition metal complexes (Fig. 1) are known to give σ-bonded oxidative addition products which can be converted into carbene complexes by H–X addition [8–10]. We report here the synthesis and the crystal structure of chloro{6-[[chloro(triphenylphosphine)platinum]-(mesitylimino)methyl-κ-C]pyridin-2-yl-κ-N}bis(triphenylphosphine)-platinum(II), **3**.



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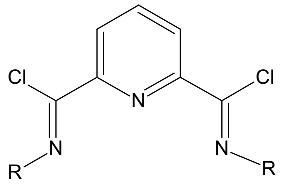

B

2. Experimental

2.1. Materials and method

All manipulations were performed under argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were obtained on a Varian As 400 MHz spectrometer. The C, H and N analyses were performed using a CHNS-932 (LECO) instrument at the Technical and Scientific Research Council of Turkey, TUBITAK. Pyridine-2,6-dicarboxylic acid (Fluka) and 2,4,6-trimethylaniline (Aldrich) were used as received. $[Pt(PPh_3)_4]$ and **1** were prepared using a literature method [11,12]. Solvents were of analytical grade and were distilled after drying.

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doi:10.1016/j.poly.2008.09.019

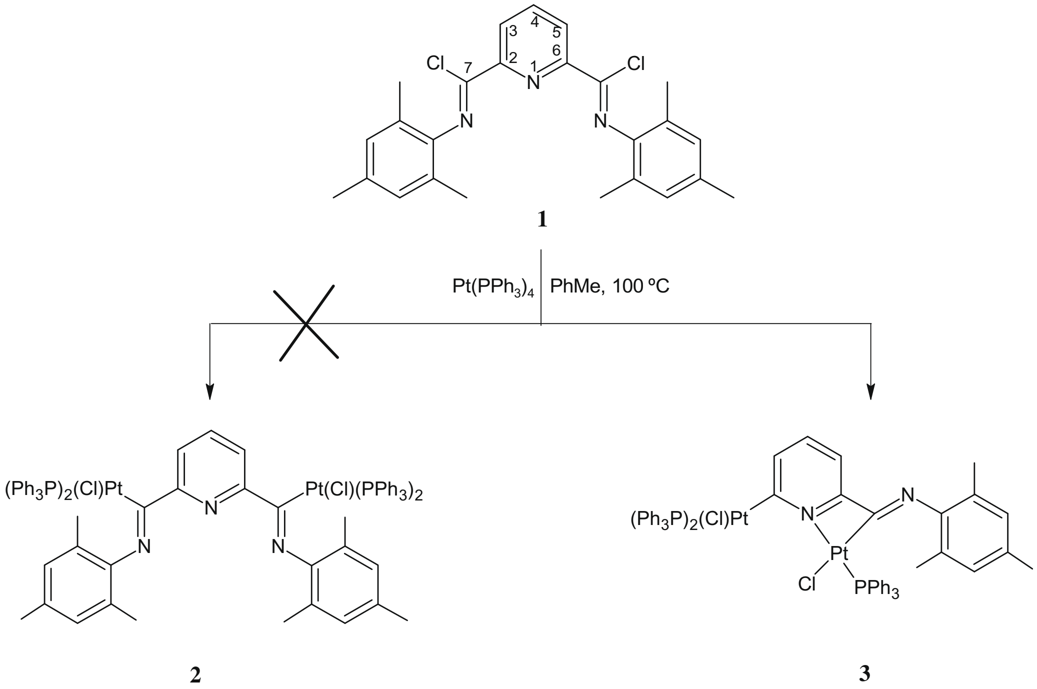

Fig. 1. Reaction of imidoyl chlorides with low valent transition metal complexes.

2.2. Synthesis of the title complex and analytical characterization

2.2.1. Synthesis of **3**

A mixture of *N*,*N′*-bis(2,4,6-trimethylphenyl)pyridine-2,6-carboxyimidoyl dichloride (88 mg, 0.2 mmol) and [Pt(PPh$_3$)$_4$] (500 mg, 0.4 mmol) in toluene (20 mL) was stirred under argon for 2 h at 100 °C. After cooling, the solvent was removed *in vacuo* and the waxy residue was suspended in pentane and stirred for 1 h at ambient temperature to form a fine powder. The pentane was discarded and the residue was extracted with pentane to remove the remaining PPh$_3$. The crude product was then recrystallized from CH$_2$Cl$_2$ to precipitate impurities. After filtration, crystallization of the product was induced by slowly diffusing pentane into the CH$_2$Cl$_2$ solution to afford the complex as a light brown crystals.

Yield: 0.210 g (63%). *Anal.* Calc. for $C_{69}H_{59}Cl_2N_2P_3Pt_2$: C, 56.37; H, 4.04; N, 1.91. Found: C, 57.06; H, 3.57; N, 2.38%. ^{1}H NMR (δ in ppm, 400 MHz, *J* in Hz, CDCl$_3$): 1.58 (s, 6H, *o*-CH$_3$-Mes), 2.14 (s, 3H, *p*-CH$_3$-Mes), 6.6 (s, 2H, *CH*-Mes), 7.43 (m, 18H, *oH*-P*Ph*$_3$), 7.73 (m, *pH*-P*Ph*$_3$, 9H), 7.82 (m, *H*-Py and *mH*-P*Ph*$_3$, 21H) ^{13}C NMR (δ in ppm, 101 MHz, CDCl$_3$): 14.21, 18.74, 127.79, 127.85, 128.37, 128.42, 128.49, 128.54, 129.19, 129.83, 130.73, 131.17, 132.04, 134.12, 134.18, 134.23, 134.75, 134.81, 134.86.

Table 1
Crystal data and details of the structure refinement for the title complex.

Empirical formula	$C_{69}H_{59}N_2P_3Cl_2Pt_2$
Formula weight	1470.17
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	11.9074(5)
b (Å)	12.1059(5)
c (Å)	25.7888(10)
α (°)	96.294(3)
β (°)	93.269(3)
γ (°)	117.350(3)
V (Å^3)	3257.6(3)
Z, D_{calc} (g/cm^3)	2, 1.499
μ (Mo Kα) (mm^{-1})	4.485
F(000)	1444
Crystal size (mm^3)	0.60 × 0.36 × 0.18
Absorption correction	integration
θ Range for data collection (°)	1.60–26.15
Reflections collected/unique (R_{int})	58735/12790 (0.045)
Data/restrain/parameters	10093/0/703
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.0310/R_w = 0.0762$
R indices (all data)	$R = 0.0423/R_w = 0.0791$
Goodness-of-fit (GoF) on F^2	0.993
Highest peak/deepest hole (eÅ^{-3})	2.210/−1.231

2.3. Crystal structure determination

Light brown single crystals suitable for data collection were mounted on a glass fibre and the diffraction intensity data were collected at room temperature on a STOE IPDS 2 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A summary of crystallographic data and details of the structure refinement are listed in Table 1. The cell parameters were determined by using X-AREA software [13] on the setting angles of 58735 reflections [1.60° < θ < 26.15°]. Absorption correction was achieved by the integration method via X-RED software [13]. A total of 58735 reflections were collected for $h_{min} = -14$, $h_{max} = 14$, $k_{min} = -14$, $k_{max} = 14$, $l_{min} = -31$, $l_{max} = 31$. The crystal structure was solved by SHELXS-97 [14]. The refinement (on F^2) was carried out by full-matrix least square techniques using the SHELXL-97 program [15]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms, with C–H distances of 0.93 Å for aromatic H atoms and 0.96 Å for methyl H atoms.

Examination of the structure of the title compound with PLATON [16] showed that there was a solvent-accessible void (380 Å^3) in the region around (1/2, 1/2, 1). The reflection (*hkl*) data were modified using the SQUEEZE option of PLATON. Although the empty space seemed large enough to accommodate small solvent molecules, the spaces are too constricted to hold any molecule larger than water. Since no water was present during the synthesis or recrystallization, and since little electron density in the area of the void was found, we conclude that the voids are empty.

3. Results and discussion

Pyridine-2,6-dicarboxyimidoyl dichloride (**1**) is an interesting diimidoyl chloride that has been reported recently. Keeping the above mentioned facts in mind and in continuation of our study with aminocarbene complexes [17], we treated **1** with tetrakis(triphenylphosphine)platinum(0) in toluene at 100 °C for 2 h with the hope of obtaining **2**. The easy cleavage of the C_2–C_7 bond implies that this bond is probably the weakest bond in **1**. However, ^{1}H NMR solution studies on the crystalline light brown solid revealed the presence of a pyridine skeleton with one mesityl substituent. In order to determine the atom connectivity we performed a crystallographic study which confirmed unequivocally the structure depicted as **3**. The mechanistic details of the cleavage reaction are not fully understood.

In summary, pyridine-2,6-dicarboxyimidoyl dichloride (**1**) experiences complex transformations when reacted with [Pt(PPh_3)$_4$]. The mechanistic aspect of this process remains to be elucidated.

An ORTEP3 [18] view of the title complex is shown in Fig. 2. The title compound crystallizes in the triclinic space group $P\bar{1}$.

The asymmetric unit contains one neutral binuclear complex. The coordination environments of the Pt centres are different. The coordination geometry around Pt1 atom is distorted square-planar, formed by the C and N atoms of the platinalactam ring, Cl atom and P atom from the triphenylphosphine group. The N1–Pt1–C1 angle is acute, with a value of 66.68(15)°, but is comparable to those found in similar metallalactam complexes [19–21]. The Cl1–Pt1–P1 angle is more obtuse [97.17(4)°] to accommodate the steric bulk of the PPh_3 ligand. The maximum deviation of the coordination plane formed by the Pt1/Cl1/C1/N1/P1 atoms is −0.050 Å for Pt1. The Pt2 atom has the expected square-planar geometry, involving one Cl atom, the coordinating C atom of the pyridine ring and two P atoms from the triphenylphosphine groups, with no atom deviating by more than 0.077 Å [for Pt2] from the coordination plane defined by Pt2/Cl2/P2/P3/C2. The coordination planes are almost perpendicular to each other [88.12(5)°].

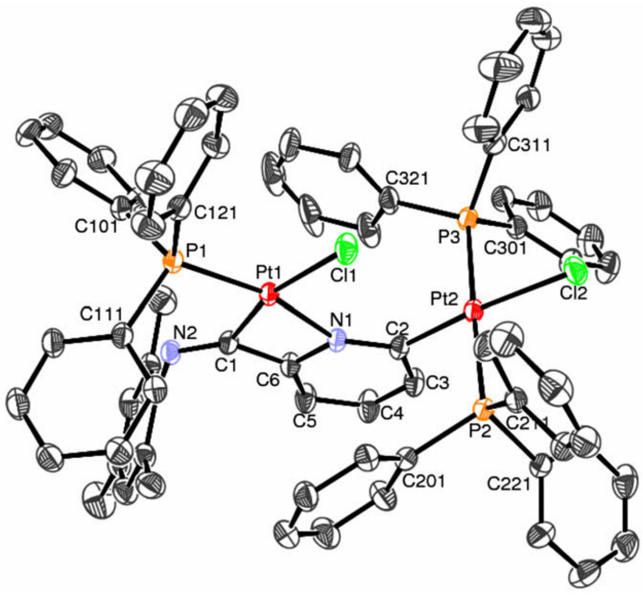

Fig. 2. An ORTEP3 view of the title compound. Displacement ellipsoids are shown at the 20% probability level and hydrogen atoms have been omitted for clarity.

Table 2
Selected geometrical parameters (Å, °) for the title complex.

Pt1–Cl1	2.374(1)	Pt2–Cl2	2.381(1)
Pt1–C1	1.984(5)	Pt2–C2	1.992(5)
Pt1–N1	2.105(3)	N2–C1	1.278(5)
N1–C6	1.367(6)	C1–C6	1.486(6)
N2–C7	1.423(6)	N1–C2	1.324(5)
N1–Pt1–Cl1	98.86(10)	C2–Pt2–P3	89.77(13)
P1–Pt1–Cl1	97.17(4)	C2–Pt2–P2	90.58(13)
N1–Pt1–P1	163.58(10)	P3–Pt2–Cl2	90.10(5)
C1–Pt1–Cl1	165.16(12)	P2–Pt2–Cl2	89.20(4)
C6–C1–Pt1	95.3(3)	P3–Pt2–P2	177.25(4)
C6–N1–Pt1	94.0(2)	C2–Pt2–Cl2	172.62(12)
N2–C1–Pt1	134.0(3)	N1–C2–Pt2	125.0(3)
C2–N1–Pt1	143.0(3)	C3–C2–Pt2	118.3(3)
C1–N2–C7	122.3(4)		

The Pt–P and Pt–N coordination distances are in the expected range and are in accordance with other reported Pt structures [19,22–24]. Selected interatomic distances, bond and torsion angles for the title complex are listed in Table 2.

The mesityl ring is rotated with respect to the platinalactam ring (Pt1/N1/C1/C6) plane by 89.5(3)°. The Pt2-P2 and Pt2-P3 bonds [2.298(1) and 2.297(1) Å] are significantly longer than the Pt1–P1 bond *trans* to the platinalactam N atom [2.216(1) Å]. This difference appears to be a result of a stronger *trans* influence of the P atom.

In the crystal structure, the molecules of the title compound are linked by C–H⋯N weak hydrogen bonds into centrosymmetric dimers, as shown in Fig. 3. The C113 atom in the molecule at (x,y,z) acts as a weak hydrogen-bond donor, via atom H113, to the N2 atom at ($1-x$,$1-y$,$1-z$), thus forming a dimer characterized by an $R_2^2(16)$ motif [25] with an inversion centre at (1/2,1/2,1/2) with

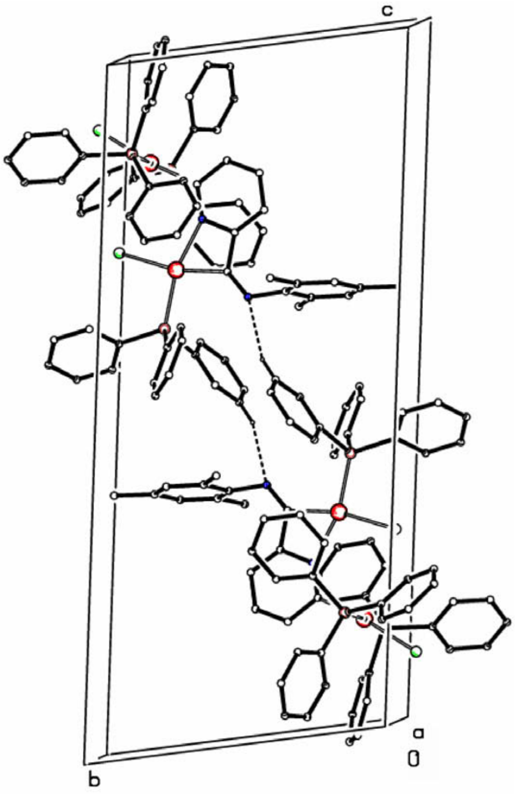

Fig. 3. Part of the crystal structure of the title compound showing the centrosymmetric dimer containing the $R_2^2(16)$ ring. For the sake of clarity, all H atoms except H113 have been omitted.

dimensions $H113\cdots N2^a = 2.62$ Å, $C113\cdots N2^a = 3.505(7)$ Å and $\angle C113{-}H113\cdots N2^a = 160^\circ$ (a: $1-x, 1-y, 1-z$).

4. Supplementary data

CCDC 666496 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under Grant No. F279 of the University Research Fund) and Dokuz Eylül University Research Funds (Project No.: 04.KB.FEN.100).

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