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DICHLOROTRIETHYLPHOSPHINE-[*N*-FORMYL-*N*,*N*′-bis(3,4-DIMETHOXY)BENZYL-TRIMETHYLENEDIAMINE]PLATINUM(II)

O. Şahin[1], E.Ö. Özcan[2], N. Gürbüz[2], İ. Özdemir[2], O. Büyükgüngör[3]

[1]*Scientific and Technological Research Application and Research Center, Sinop University, Sinop, Turkey*
  E-mail: onurs@sinop.edu.tr
[2]*Department of Chemistyr, İnönü University, Malatya, Turkey*
[3]*Department of Physics, Ondokuz Mayıs University, Samsun, Turkey*

By treatment of 1,3-bis(3,4-dimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (**1**) with KOBu^t and [PtCl$_2$(PEt$_3$)$_2$]$_2$ *N*-coordinated platinum complex (**2**) is obtained. The Pt atom is coordinated in square planar arrangements by two chloride ions in a *trans*-configuration, the *N*-formyl-*N*,*N*′-bisaryltrimethylenediamine nitrogen atom, and the phosphine P atom. An extensive three-dimensional network of three C—H⋯O hydrogen bonds, two C—H⋯π and one π⋯π interactions are responsible for the crystal stabilization. Intermolecular hydrogen bonds and C—H⋯π interactions produce $R_2^2(6)$, $R_2^2(22)$, $R_2^2(24)$, $R_3^3(23)$, $R_4^4(26)$, and $R_4^4(32)$ rings.

K e y w o r d s: tetrahydropyrimidine, *N*-formyl-*N*,*N*′-bisaryltrimethylenediamine, Pt(II) complex, X-ray diffraction analysis.

INTRODUCTION

The first metal complexes of *N*-heterocyclic carbenes (NHCs) were reported independently in 1968 by Wanzlick [1] and Öfele [2] and subsequently, electron-rich alkenes were used as a source of various NHC complexes by Lappert and co-workers [3—5]. Since the 1991 isolation and crystallographic characterization of stable of *N*-heterocyclic carbenes by Arduengo [6], increasing attention has been focused on using these compounds as ancillary ligands for transition metal complexes [7, 8]. Last few decades have witnessed an extensive exploration of metal-NHC complexes as catalysts for a wide variety of organic transformations, including olefin metathesis [9], hydrosilylation [10], hydroformylation [11, 12], hydrogenation [13, 14], C—C [15—17] and C—N [18] coupling reactions. The ancillary ligand (NHC) coordinated to the metal center has a number of important roles in homogeneous catalysis such as providing a stabilizing effect and governing activity and selectivity. The number, nature, and position of substituents on the nitrogen atom(s) and/or the NHC ring have been found to play a crucial role in tuning the catalytic activity. Whilst many modifications to the five-membered ring of the ligand aryl substituent have been described, relatively little attention has been paid to the effect of the ring size [19].

For the present study, we selected 3,4,5,6-tetrahydropyrimidinium salts. This choice was guided by several considerations. An important characteristic of the carbene ligands in active complexes is their strong-electron donating effect, primarily a σ-effect. Due to their six-membered ring geometry, tetrahydopyrimidine-2-ylidenes are stronger σ-donating ligands when compared to five-membered analogues [19]. Treatment of 1,3-bis(3,4-dimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride

(**1**) with KOBu^t in THF led initially to the corresponding *N*-formyl-*N*,*N*′-bisaryltrimethylenediamine, and by the addition of [PtCl$_2$(PEt$_3$)$_2$]$_2$, *N*-coordinated platinum complex (**2**) was obtained. We report herein the X-ray crystal structure of **2**.

EXPERIMENTAL

Materials and measurements. All reactions were carried out under Ar in flame-dried glass-ware using the standard Schlenk-type flasks. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK). The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et$_2$O (Na/K alloy), C$_2$H$_5$OH (Mg). Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Mercury spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in CDCl$_3$ with tetramethylsilane as the internal reference.

Synthesis. A suspension of 1,3-bis(3,4-dimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (1.1 mmol) and KOBu^t (1.2 mmol) in THF (20 ml) was stirred at room temperature for 12 h and volatiles were removed under vacuum. Toluene (20 ml) was added and the suspension was filtrated. After the removal of toluene from the filtrate, colorless oil was obtained. This compound (1 mmol) and [PtCl$_2$(PEt$_3$)$_2$]$_2$ (0.5 mmol) was heated under reflux in degassed toluene (20 ml) for 3 h. The reaction mixture was then filtered while hot, and the volume was reduced to about 10 ml before the addition of *n*-hexane (15 ml). The precipitate formed was crystallized from CH$_2$Cl$_2$/diethylether (5:15 ml) to give the complex as yellow crystals. Yields: 0.59 g 75 %. m.p.: 163—164 °C. ^{1}H NMR (CDCl$_3$) δ = 1.11 (t, 9H, *J* = 7.56 Hz, P(CH$_2$C*H$_3$*)$_3$), 1.72—1.90 (m, 6H, P(C*H$_2$*CH$_3$)$_3$), 1.97—2.08 (m, 2H, NCH$_2$C*H$_2$*CH$_2$N), 3.01—3.50 (m, 4H, NC*H$_2$*CH$_2$C*H$_2$*N), 3.86; 3.87; 3.88 and 3.89 (s, 12H, CH$_2$C$_6$H$_3$-3,4-(OC*H$_3$*)$_2$), 4.20—4.83 (m, 4H, NC*H$_2$*C$_6$H$_3$-3,4-(OCH$_3$)$_2$), 6.70—7.29 (m, 6H, CH$_2$C$_6$*H$_3$*-3,4-(OCH$_3$)$_2$), 8.34 (s, 1H, C*H*O). ^{13}C NMR (CDCl$_3$) δ = 7.6 (P(CH$_2$*C*H$_3$)$_3$), 13.9 (P(*C*H$_2$CH$_3$)$_3$), 14.4 (NCH$_2$*C*H$_2$CH$_2$N), 38.7 and 42.2 (N*C*H$_2$CH$_2$*C*H$_2$N), 55.8; 55.9; 56.0 and 56.2 (CH$_2$C$_6$H$_3$-3,4-(O*C*H$_3$)$_2$), 47.7 and 58.4 (N*C*H$_2$C$_6$H$_3$-3,4-(OCH$_3$)$_2$), 110.5; 110.8; 110.9; 111.4; 113.5; 120.2; 122.7; 128.2; 128.7; 148.7; 148.8; 149.0 and 149.4 (CH$_2$*C*$_6$H$_3$-3,4-(OCH$_3$)$_2$), 163.3 (*C*HO). Anal. Calc. for C$_{28}$H$_{46}$Cl$_2$N$_2$O$_5$PPt: C, 42,70; H, 5.89; N, 3.56 %. Found: C, 42,39; H, 5.95; N, 3,71 %.

Crystallography. A yellow color crystal of the platinum complex, suitable for data collection was mounted on a glass fiber and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated MoK_α radiation at 296 K. The structure was solved by direct methods using SHELXS-97 [20] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 from within the WINGX [21] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in calculated positions (C—H = 0.93—0.97 Å and N—H = 0.91 Å) and treated using a riding model with U = 1.2 times the U value of the parent atom for NH, CH, CH$_2$, and CH$_3$. The molecular drawing was obtained using ORTEP-III [22]. Geometric calculations were performed on PLATON [23]. Atomic coordinates have been deposited to the Cambridge Structural Database (http://www.ccdc.cam.ac.uk): CCDC 822813.

RESULTS AND DISCUSSION

Dichlorotriethylphosphine-[*N*-formyl-*N*,*N*′-bis(3,4-dimethoxy)benzyltrimethylene-diamine]-platin(II). The *in situ* deprotonation of azolium salt to produce the desired *N*-heterocyclic carbene has the advantage that carbene does not have to be isolated, thus simplifying the reaction workups when the aim is the preparation of the metal complex [24—26]. In this study, treatment of 1,3-bis(3,4-dimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride with KOBu^t in THF led initially to the corresponding *N*-aryl-*N*-formyl-*N*′-aryltrimethylenediamin, but it could not yield carbene (Fig. 1). A similiar behavior was previously observed for 1,2-diaryl-3-methyltetrahydropyrimidinium [27—29]. By treatment of *N*-aryl-*N*-formyl-*N*′-aryltrimethylenediamin with [PtCl$_2$(PEt$_3$)$_2$]$_2$, *N*-coordinated platinum complex (**2**) was obtained.
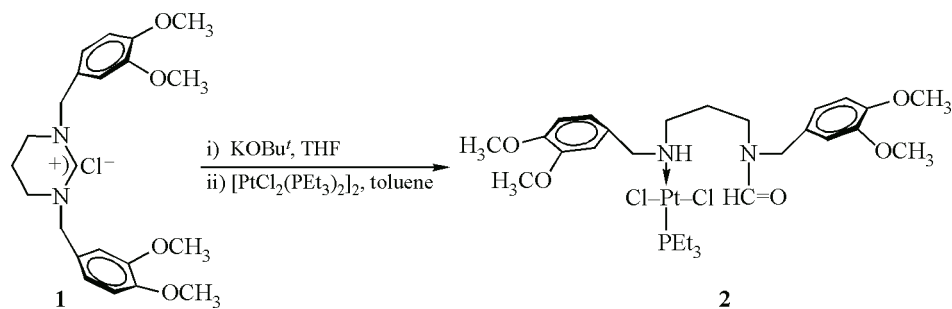
Fig. 1. Synthesis of compound **2**

X-ray structural determination. A summary of the crystal data, experimental details, and refinement results is listed in Table 1. The corresponding ORTEP view with the atom numbering scheme is shown in Fig. 2. Details of hydrogen bonds and C—H···π interactions are given in Table 3. In the complex, the N-bonded *N*-formyl-*N,N′*-bisaryltrimethylenediamine ligand is monodentate and the coordination around the platinum(II) atom is completed by a phosphorus and two chloride ions, with the four ligands being arranged in a *trans*-distorted square planar geometry. The Pt—P distances in several complexes reported in the literature [30, 31], as in this work, do not vary appreciably whether the phosphorus atoms are *trans* to chlorine or nitrogen or not. The Pt—Cl distances (Pt(1)—Cl(1) = = 2.2984(7) Å and Pt(1)—Cl(2) = 2.2994(7) Å) are within the expected range, as are their Pt—P (2.2286(8) Å) and Pt—N (2.147(2) Å) bond distances. As Table 2 shows, these values are not significantly different from those found in the related complexes [32, 33]. The values of the Cl(1)—Pt(1)—Cl(2), N(1)—Pt(1)—P(1), P(1)—Pt(1)—Cl(1), and P(1)—Pt(1)—Cl(2) angles are 176.38(3)°, 176.29(6)°, 88.62(3)°, and 94.51(3)° respectively. Least-squares mean plane calculations for benzene

T a b l e   1

Crystal and refinement data for **2**

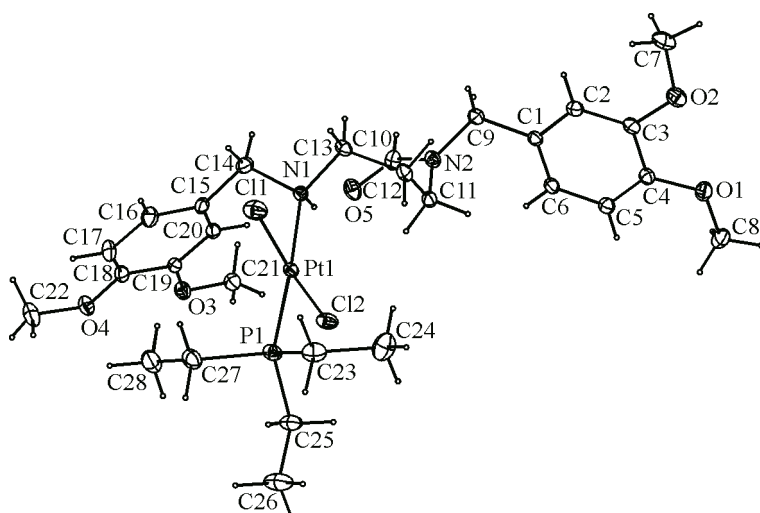| Molecular formula	$C_{28}H_{45}Cl_2N_2O_5PPt$
Molecular mass	786.62
Crystal system	Triclinic
Space group	*P*-1
Unit cell parameters *a, b, c*, Å	7.9503(3), 14.3686(6), 15.2248(6)
α, β, γ, deg.	76.197(3), 74.646(2), 88.426(3)
V, Å^3	1627.51(11)
Z	2
ρ_{calc}, g/cm^3	1.605
T, K	293
Radiation; λ, Å	MoK_α; 0.71073
Crystal size, mm	0.47×0.35×0.11
Reflections measured	21333
$\theta_{min, max}$, deg.	1.5—28.1
Independent reflections	7406 [R_{int} = 0.023]
Parameters refined	352
Final *R* factor [$I > 2\sigma(I)$]	*R*1 = 0.022, *wR*2 = 0.050
R factor (all data)	*R*1 = 0.026, *wR*2 = 0.051
GOOF	1.07
Residual electron density (min / max), e/Å^3	−1.03 / 0.40

Fig. 2. Molecule of **2** showing the atom numbering scheme.
Displacement ellipsoids are drawn at the 30 % probability level

T a b l e   2

Selected bond lengths (Å)
and angles (deg.) *for* **2**

Pt(1)—N(1)	2.147(2)
Pt(1)—P(1)	2.2286(8)
Pt(1)—Cl(1)	2.2984(7)
C(10)—O(5)	1.218(4)
Pt(1)—Cl(2)	2.2994(7)
N(1)—Pt(1)—Cl(2)	87.40(6)
Cl(1)—Pt(1)—Cl(2)	176.38(3)
P(1)—Pt(1)—Cl(1)	88.62(3)
N(1)—Pt(1)—P(1)	176.29(6)
N(1)—Pt(1)—Cl(1)	89.58(6)
P(1)—Pt(1)—Cl(2)	94.51(3)

ring (C(1)—C(6) and C(15)—C(20)) planes show that they are approximately planar with respective maximum deviations of 0.0117(21) Å for C(3) and 0.0185(22) Å for C(18). The dihedral angle between the benzene rings is 48.99(12)°.

Molecules of **I** are linked into sheets by a combination of C—H···O hydrogen bonds (Table 3). Within the selected asymmetric unit, the intramolecular N(1)—H(1)···O(5) hydrogen bond produces the S(8) motif [34]. The C(8) atom in the molecule at (x, y, z) acts as a hydrogen bond donor via the H(8B) atom to the O(5) atom in the molecule at (–x, –y, –z), thus forming a centrosymmetric $R_2^2(22)$ ring centered at (0, 0, 0). Similarly, the C(21) atom in the molecule at (x, y, z) acts as a hydrogen bond donor via the H(21A) atom to the O(3) atom in the molecule at (–x+1, –y, –z+1), thus forming a centrosymmetric $R_2^2(6)$ ring centered at (1/2, 0, 1/2). The C(22) atom in the molecule at (x, y, z) acts as a hydrogen bond donor via the H(22A) atom to the O(1) atom in the molecule at (x+1, y, z+1), thus forming a C(19) chain running parallel to the [101] direction. The combination of intermolecular C—H···O hydrogen bonds generates a chain of edge-fused $R_2^2(6)R_3^3(23)R_2^2(22)R_3^3(23)$ rings running parallel to the [101] direction (Fig. 3).

T a b l e   3

Hydrogen bonds and C—H···π *interactions for* **2**

D—H···A	D—H, Å	H···A, Å	D···A, Å	D—H···A, deg.	Symmetry operations
N(1)—H(1)···O(5)	0.91	2.19	3.008(3)	149	x, y, z
C(8)—H(8B)···O(5)	0.96	2.62	3.273(5)	126	$-x, -y, -z$
C(21)—H(21A)···O(3)	0.96	2.56	3.370(4)	142	$-x+1, -y, -z+1$
C(22)—H(22A)···O(1)	0.96	2.60	3.482(5)	152	$x+1, y, z+1$
X···H(I)	Cg(J)	H···Cg, Å		X—H···Cg, deg.	Symmetry operations
C(8)—H(8A)	Cg(2)^{iv}	3.0936		117	$x, y, z-1$
C(23)—H(23B)	Cg(1)^{v}	3.2897		157	$-x, -y+1, -z$

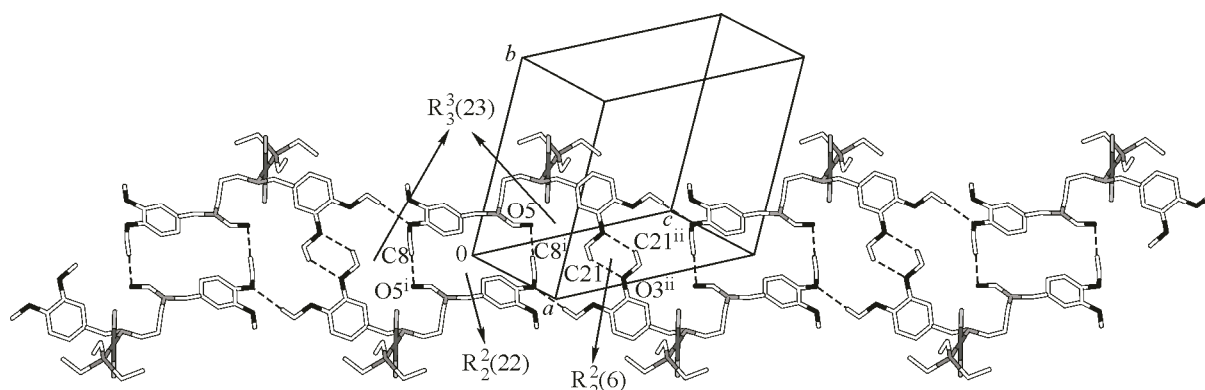Cg(1): C(1)—C(2)—C(3)—C(4)—C(5)—C(6), Cg(2): C(15)—C(16)—C(17)—C(18)—C(19)—C(20).

Fig. 3. Part of the crystal structure of **2**, showing the formation of a chain of edge-fused
$R_2^2(6) R_3^3(23) R_2^2(22) R_3^3(23)$ rings. (Symmetry codes as in Table 3)

Compound **2** also contains two C—H$\cdots\pi$ and one $\pi\cdots\pi$ interactions. In the first, the C(8) atom in the molecule at (x, y, z) acts as a hydrogen bond donor to the C(15)—C(20) benzene ring in the molecule at $(x, y, z-1)$, thus forming a chain running parallel to the [001] direction. In the second, the C(23) atom in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C(1)—C(6) benzene ring in the molecule at $(-x, -y+1, -z)$, thus forming a centrosymmetric $R_2^2(24)$ ring centered at (0, 1/2, 0). Details of these interactions are given in Table 3. An intermolecular $\pi\cdots\pi$ contact occurs between the two symmetry-related C(1)—C(6) benzene rings of the neighboring molecules. The Cg(1) ring is oriented in such a way that the perpendicular distance from Cg(1) to Cg(1)^{vi} is 3.557 Å (symmetry code: (vi) $-x-1, -y, -z$). The distance between the ring centroids is 3.6638(18) Å. The combination of C—H$\cdots\pi$ and $\pi\cdots\pi$ interactions generates a chain of edge-fused $R_2^2(24) R_4^4(26) R_4^4(32)$ rings running parallel to the [111] direction (Fig. 4).

Conclusions. The above results show the 1,3-bis(3,4-dimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride ligands to give the corresponding propandiamin derivative on reaction with KOBu^t.
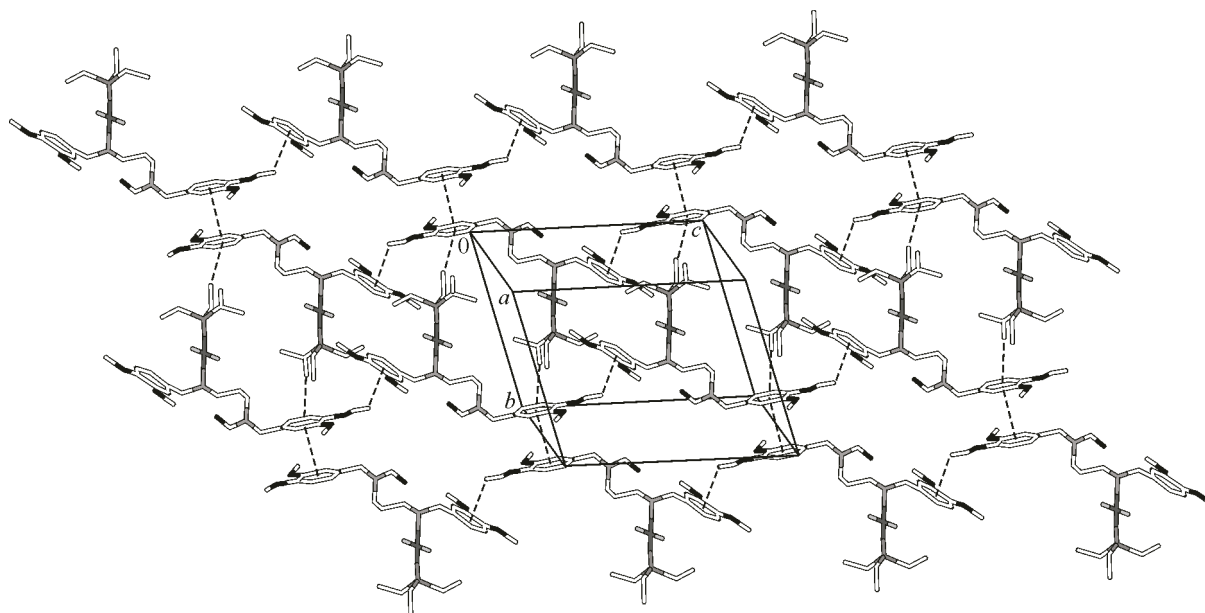

Fig. 4. Part of the crystal structure of **2** showing the formation of a chain along [111] generated by C—H$\cdots\pi$ and
$\pi\cdots\pi$ stacking interactions

The *N*-coordinated platinum complex was obtained by the reaction of the resulting propandiamin derivative and [PtCl$_2$(PEt$_3$)$_2$]$_2$. X-ray data of the compound confirmed the structure.

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