

Note

Stabilization of the (η^4 -COD)Pt-fragment (COD = η^2, η^2 -cyclo-octa-1,5-diene) by a bistriazenide: Synthesis and X-ray structural characterization of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$, a neutral 1,2-bis(phenyltriazenido)benzene complex of platinum(II)

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Abstract

After exchange of Cl against NO₃ by reaction with AgNO₃ $[(\text{COD})\text{PtCl}_2]$ reacts with the sodium salt of 1,2-bis(phenyltriazeno)benzene to give $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$, the first example of a π -fragment of platinum(II) stabilized by two symmetrical triazenide chains. The new complex belongs to the monoclinic space group $C2/c$ and corroborates the ability of the (COD)Pt fragment to be stabilized by bidentate ligands. The odd *flying dragon* structure of the title compound retains the C_{2v} symmetry of the free anion 1,2-bis(phenyltriazenido)benzene.

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1. Introduction

Organoplatinum(II) complexes $[(\text{COD})\text{Pt}(\text{R})_2]$ (R = alkyl or aryl) are well known since decades and have been widely used as precursors for mono- and polynuclear organometallic platinum(II) compounds [1–10]. They are also of interest for the generation of organoplatinum reaction centres on catalyst surfaces for heterogeneous catalysis [11] or as potential precursors for chemical vapour deposition (CVD) of platinum [12]. In contrast, with exception of some classical examples like $[(\text{COD})\text{PtCl}_2]$ [13], a very

small number of complexes is known in which the (COD)Pt fragment is stabilized by an heteroatom. There are only six crystallographically characterized [14–19] examples of compounds with two nitrogen atoms acting as co-ligands, like for example (η^2, η^2 -cyclo-octa-1,5-diene)-bis(3,5-bis(trifluoromethyl)pyrazole-*N*)-platinum(II) [14] and (*N,N'*-1,2-phenylenebis(benzenesulfonamido))(η^2, η^2 -cyclo-octa-1,5-diene)-platinum(II) [15].

None of the described examples exhibits a triazene chain as co-ligand. On the basis of their structures and biological activity [20], triazenes are well important and interesting substances. As ligands, the N–N–N moieties – with single or twofold nitrogen chains, neutral or anionic (triazenides) – can act as mono, bidentate or chelate ligands, showing a remarkable ability to support the stereochemical requisites of a wide variety of metal transition complexes [21–23].

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¹ In memoriam.

With the aim, to investigate alternative ways to stabilize the (COD)Pt fragment, as well as the ability of double-chained triazenes to act as co-ligands in this compound type, we report the synthesis and the X-ray characterization of metallacyclic $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$, the first π -fragment of platinum(II) stabilized by two symmetrical triazenide chains, which achieve a heterocyclic five-membered ring with the metallic center. There is only one comparable complex reported up to date [15].

2. Experimental

All manipulations were carried out under nitrogen by use of standard Schlenk techniques.

2.1. $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$, $[(\eta^2, \eta^2\text{-cyclo-octa-1,5-diene})\text{bis}(\text{phenyltriazene})\text{-benzene-platinum(II)}]$

1,2-Bis(phenyltriazene)benzene (85.4 mg, 0.27 mmol) was dissolved in 15 ml of absolute tetrahydrofuran and treated with small portions of metallic sodium powder until H_2 evolution stopped. The resulting intense-red mixture was filtered to remove excess of metallic sodium. $\text{C}_8\text{H}_{12}\text{PtCl}_2$ (101.0 mg, 0.27 mmol) was dissolved in 15 ml of absolute tetrahydrofuran and treated with a solution of 91.7 mg (0.54 mmol) AgNO_3 in 10 ml of absolute acetonitrile. The resulting mixture was filtered to remove the precipitate of AgCl . To this solution the intense-red mixture was added slowly with continuous stirring. After stirring at room temperature for 3 h, a dark-gray precipitate was filtered off. The combined organic solvents were evaporated. The resulting orange solid was dried in vacuo. Orange prism-shaped single crystals suitable for X-ray diffraction were obtained at room temperature within two weeks by slow diffusion of *n*-hexane into a THF solution of the title complex.

Properties: air stable, crystalline substance; $\text{C}_{26}\text{H}_{26}\text{N}_6\text{Pt}$ (617.62); Yield: 148.2 mg (0.24 mmol), 89% based on $\text{C}_8\text{H}_{12}\text{PtCl}_2$. Melting point: 96 °C.

IR (KBr): the typical band observed at 1412.7 for the free ligand (m, $\nu_{\text{as}}(\text{N}=\text{N})$) is substituted for a stretching at 1259.8 cm^{-1} in the spectrum of the complex (decreasing of the N–N bond order of the ligand). The band at 3292.8 cm^{-1} in the spectrum of the free ligand (m, $\nu_{\text{as}}(\text{N}=\text{H})$) is suppressed in the spectrum of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$.

2.2. Crystallography

X-ray data were collected with a STOE-IPDS diffractometer. The structure of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$ was solved by direct methods (SHELXS-97) [24]. Refinements were carried out with the SHELXL-97 [25] package. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

3. Results and discussion

In the X-ray studies of the monoclinic title complex the space group $C2/c$ was chosen on the basis of statistics and later justified by the successful refinements. Crystal data and experimental conditions are given in Table 1. Selected

Table 1
Crystal data and structure refinement for $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$

Empirical formula	$\text{C}_{26}\text{H}_{26}\text{N}_6\text{Pt}$
Formula weight	617.62
T (K)	293(2)
Radiation	Mo $K\alpha$
λ (Å)	0.71073
Crystal system,	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	16.657(9)
b (Å)	12.048(8)
c (Å)	13.141(6)
α (°)	90
β (°)	121.24(4)
γ (°)	90
V (Å ³)	2255(2)
Z	4
Calculated density (g cm^{-3})	1.819
Absorption coefficient (mm^{-1})	6.250
$F(000)$	1208
Crystal size (mm)	$0.2 \times 0.04 \times 0.02$
θ Range (°)	3.30–25.49
Index ranges	$-20 \leq h \leq 20, -14 \leq k \leq 9,$ $-13 \leq l \leq 14$
Reflections collected	4833
Reflections unique [R_{int}]	1953 [0.0684]
Completeness to θ max.	93.0%
Absorption correction	Analytical
Max. and min. transmission	0.9121 and 0.3679
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1953/0/150
Goodness-of-fit on F^2	0.917
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0417, wR_2 = 0.0734$
R indices (all data)	$R_1 = 0.0716, wR_2 = 0.0794$
Largest diff. peak and hole (e Å^{-3})	0.749 and -0.661

Table 2
Selected bond lengths (Å) and angles (°) for $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$

<i>Bond lengths</i> (Å)	
Pt(1)–N(11)	2.025(8)
Pt(1)–C(31)	2.163(11)
Pt(1)–C(34)	2.193(10)
N(11)–N(12)	1.364(10)
N(11)–C(11)	1.418(12)
N(12)–N(13)	1.252(11)
N(13)–C(21)	1.404(12)
<i>Bond angles</i> (°)	
N(11)#1–Pt(1)–C(31)#1	160.0(3)
N(11)–Pt(1)–C(31)#1	97.3(4)
N(11)#1–Pt(1)–C(34)	163.3(3)
N(11)–Pt(1)–C(34)	98.3(3)
C(11)–N(11)–Pt(1)	114.5(6)
C(11)#1–C(11)–N(11)	115.6(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$.

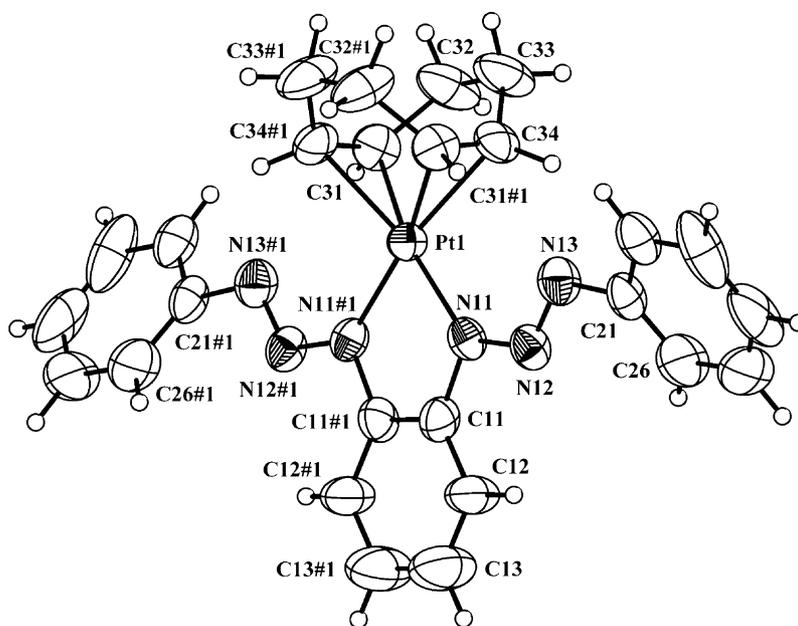


Fig. 1. ZORTEP [26] plot with atom-labeling scheme of the molecular structure of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$; displacement ellipsoids at the 50% level. Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$.

bond distances and angles of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$ are listed in Table 2; Fig. 1 displays the ZORTEP [26] representation of the molecule.

The main structural feature of $[(\eta^4\text{-COD})\text{Pt}(\text{NNN-Ph})_2\text{C}_6\text{H}_4]$ is a unique “flying dragon” conformation, which retains the C_{2v} symmetry of the free anion 1,2-bis(phenyl-triazenide)benzene. The molecule contains a twofold axis bisecting the central phenyl ring of the triazenido ligand, the Pt atom and the COD ligand. The $\eta^2\text{-C-Pt}$ bonds are not fully symmetrical, showing distances of 2.163(11) {Pt(1)–C(31)} and 2.193(10) Å {Pt(1)–C(34)}. The Pt–N bonds {Pt(1)–N(11) and Pt(1)–N(11)#1} measure 2.025(8) Å. Like in other complexes containing the COD–Pt fragment, the platinum atom has a highly distorted octahedral geometry. The substitution of the two Cl^- ligands in $[(\text{COD})\text{PtCl}_2]$ by two N atoms of the triazenide chains generates a heterocyclic five-membered PtN_2C_2 ring incorporating the metallic centre. This confirms the relatively high stability of the 12-electrons fragment $(\text{COD})\text{Pt}(\text{II})$ as well its affinity towards bidentate ligands, to some extent comparable to the dienophilic character of the 14-electrons system $\text{Fe}(\text{CO})_3$.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC No. CSD 283602. Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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