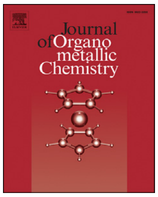
Journal of Organometallic Chemistry 828 (2017) 30–37

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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



Review

Organophosphines in organoplatinum complexes: Structural aspects of $PtPC_2X$ ($X = H, O, N, B, Cl, S$ or I) derivatives

Milan Melník [a, b, *], Peter Mikuš [a, b]

[a] *Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic*
[b] *Toxicological and Antidoping Center, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic*

ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form
28 October 2016
Accepted 4 November 2016
Available online 5 November 2016

Keywords:
Structure
Organoplatinum
Organophosphines
Trans-influence
Isomers

ABSTRACT

In this review are summarized and analyzed structural parameters of over seventy monomeric organoplatinum complexes with $PtPC_2X$ ($X = H, O, N, B, Cl, S$ or I) inner coordination sphere. These complexes crystallized in four crystal systems: tetragonal (×2), orthorhombic (×3), triclinic (×27) and monoclinic (×41). The inner coordination spheres about platinum atoms are built by mono- P, C, H, O, N, Cl, S, I, bi- C/C, C/O, C/N, P/N, P/C, P/S, and tri- C/C/B, P/C/C, C/N/C and P/C/N- dentate ligands. There are complexes with cis- and trans-configurations from which the former by far prevails (56 examples) against (8 examples) with trans-configuration. The chelating ligands created wide variety of metallocycles with three-, four-, five-, and six-membered metallocyclic rings. There are examples which exist in isomeric forms-distortion and ligand isomerism. Several relationships were found and discussed.

Contents

1. Introduction

Systematic studies in the field of stereoselectivity of coordination as well as organometallic compounds over the last 50 years have become of increasing interest. Stereoselectivity in coordination compounds is very often related to important stereospecificity of biological systems, catalysis and stereochemical effects of technical processes. Recently we classified and analyzed structural parameters of stereoisomers of organoplatinum complexes [1]. In the chemistry of organoplatinum complexes organophosphines as soft-donor ligands are very often used. There are numerous published structural studies of such complexes. Structural parameters of mononuclear organoplatinum complexes with an inner coordination spheres: *cis*- PtP_2C_2 [2], PtP_2CX ($X = H, F$ or O) [3], PtP_2CX ($X = N$ or B) [4], *cis*- PtP_2CCl [5], *trans*- PtP_2CCl [6],

---

* Corresponding author. Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic.
E-mail address: qmelnik@stuba.sk (M. Melník).

http://dx.doi.org/10.1016/j.jorganchem.2016.11.011

PtP_2CX (X = S, Se, Si or Te) [7] and PtP_2CX (X = Br or I) [8] we analyzed and discussed. The aim of this review is classify and analyze structural parameters of monomeric organoplatinum complexes with an inner coordination sphere of $PtPC_2X$ (X = H, O, N, B, Cl, S or I). The structural parameters of $PtPC_2X$ compared and summarized with those found in the precursors [2–8]. The primary source of information was Cambridge Crystallographic Database up to the end of 2015.

2. $PtPC_2X$ derivatives

There are over seventy monomeric organoplatinum complexes with an inner coordination sphere of $PtPC_2X$ for which structural parameters are available. These complexes crystallized in four crystal systems: tetragonal (×2), orthorhombic (×3), triclinic (×27) and monoclinic (×41).

2.1. $PtPC_2X$ (X = H or O) derivatives

Colorless triclinic $[Pt(PPh_3)(CH_2CN)(C_{11}H_{14}N_2O)(H)]$ [9] is only example in which monodentate donor ligands create *cis*- $PtPC_2H$ inner coordination sphere. The Pt-L bond distances elongate in the order: 1.64(4) Å (H, trans to O) < 2.069(4) Å (C, trans to P) < 2.110(7) Å (C, trans to H) < 2.252(2) Å (P, trans to C). The *cis*- L-Pt-L bond angles open in the order: 85(1)° (C–Pt–H) < 88(1)° (H–Pt–P) < 90.0(2)° (C–Pt–C) < 96.7(1)° (C–Pt–P). The *trans*- L-Pt-L bond angles are 172.7(1)° (C–Pt–P) and 174.(1)° (C–Pt–H).

In two monoclinic complexes: $[Pt(PPh_3)(\eta^1\text{-}C_6H_5NO_2\text{-}o)(\eta^2\text{-}C_6H_5NO_2\text{-}o)]$ [10] and $[Pt(PPh_3)(\eta^1\text{-}C_9H_9N_2O_7)(\eta^2\text{-}C_9H_9N_2O_7)]Me_2CO$ [11] which are isostructural, the respective donor ligands create a distorted square-planar environment about each Pt(II) atom *cis*- $PtPC_2O$ inner coordination sphere. Structure of $[Pt(PPh_3)(\eta^1\text{-}C_9H_9N_2O_7)(\eta^2\text{-}C_9H_9N_2O_7)]$ [11] is shown in Fig. 1 as an example. The mean Pt-L bond distances elongate in the order: 1.985 Å (C(η^1L), trans to O) < 2.025 Å (C(η^2L), trans to P) < 2.140 Å (O, trans to C) < 2.320 Å (P, trans to C). Each chelating- C,O ligand forms five-membered metallocyclic ring with the mean C–Pt–O bite angle of 79.5° (CCNO). The mean values of the remaining *cis*- L-Pt-L bond angles open in the order: 92.5° (C–Pt–P) < 93.4° (O–Pt–P) < 95.0° (C–Pt–C). The mean values of *trans*- L-Pt-L bond angles are 172.2° (C–Pt–P) and 174.3° (C–Pt–O).

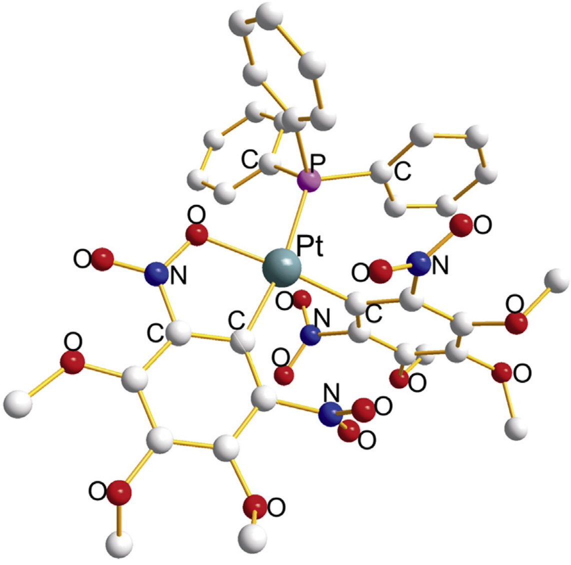


Fig. 1. Structure of $[Pt(PPh_3)(\eta^1\text{-}C_9H_9N_2O_7)(\eta^2\text{-}C_9H_9N_2O_7)]$ [11].

2.2. $PtPC_2N$ derivatives

There are over forty complexes with $PtPC_2N$ inner coordination sphere, which on the bases of combination of coordination mode of the respective donor ligands can be divided into the eight subgroups: Pt(η^1-PL)(η^1-CL)$_2$(η^1-NL); Pt(η^1-PL)(η^1-CL)(η^2-C,NL); Pt(η^2-P,NL)(η^1-CL)$_2$; Pt(η^2-P,CL)(η^1-CL)(η^1-NL); Pt(η^3-P,C,CL)(η^1-NL); Pt(η^1-PL)(η^3-C,N,CL); Pt(η^3-P,C,NL)(η^1-CL), and Pt(η^2-P,NL)(η^2-C,CL).

In two complexes with cis-configuration: tetragonal $[Pt(PPh_3)(Me)_2(\eta^1\text{-pop})]$ [12] and triclinic $[Pt(PPh_3)(Me)(\eta^1\text{-}C_{10}H_{12}N_6)(\eta^1\text{-py})](py)_2$ [13], only monodentate donor ligands are involved. The mean Pt-L bond distances elongate in the order: 2.02 Å (C, trans to N) < 2.08 Å (C, trans to P) < 2.124 Å (N, trans to C) < 2.304 Å (P, trans to C). The *cis*- L-Pt-L bond angles (mean values) open in the order: 86.4° (C–Pt–C)(C–Pt–N) < 90.7° (C–Pt–P) < 96.5° (N–Pt–P). The mean values of *trans*- L-Pt-L bond angles are 171.7° (C–Pt–N) and 176.7° (C–Pt–P).

There are nineteen examples of Pt(η^1-PL)(η^1-CL)(η^2-C,NL) type, sixteen with *cis*- $PtPC_2N$ configuration and remaining three with trans-configuration. The complexes with cis-configuration are: $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_{10}F_2N)]$ [14], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_9F_3N)]$ monoclinic [14] and triclinic [15], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_{11}ClN)]$ [16], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{15}H_{14}N)]$ [17], $[Pt(Ph_2PC_6H_4OMe\text{-}o)(Me)(\eta^2\text{-}C_{10}H_{11}N_6)]$ [18], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{20}H_{16}N\text{-}2)]$ [19], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{20}H_{16}N\text{-}4)]$ [19], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_{10}BrClN)]$ [20], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{18}H_{13}ClN)]$ [21], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{18}H_{13}ClN)]$ [21], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{17}H_{14}NS)]$ [22], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{17}H_{15}ClNO_2)]$ [23], $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{12}H_{10}NS)]$ [24], $[Pt(PPh_3)(Me)(C_6F_5)(\eta^2\text{-}C_{13}H_8N)]$ [25], and $[Pt(PPh_3)(Me)(\eta^2\text{-}C_{15}H_9BrF_4N)]$ [26].

Structure of *cis*-$[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_{10}BrClN)]$ [20] is shown in Fig. 2 as an example. The chelating ligands in the Pt(η^1-PL)(η^1-CL)(η^2-C,NL) type complexes in Refs. [14–25,27,28] create five-membered metallocyclic rings with the mean C–Pt–N bite angles

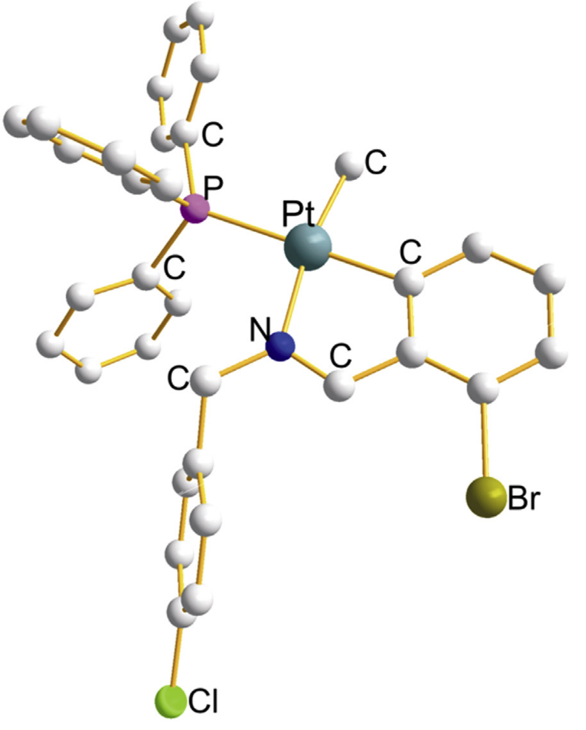


Fig. 2. Structure of *cis*-$[Pt(PPh_3)(Me)(\eta^2\text{-}C_{14}H_{10}BrClN)]$ [20].