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Heterotridentate Organomonophosphines in Pt(η^3-$P^1C^1C^2$)(Y) and Pt(η^3-$P^1C^1N^1$)(Y) Derivatives—Structural Aspects

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Abstract: This paper covers Pt(II) complexes of the compositions Pt(η^3-$P^1C^1C^2$)(Y) (Y = NL or I) and Pt(η^3-$P^1C^1N^1$)(Y), Y = OL, NL, CL, Cl or Br). These complexes crystallized in four crystal classes: monoclinic (9 examples), triclinic (3 examples), orthorhombic (3 examples), and tetragonal (2 examples). The structural parameters (Pt-L, L-Pt-L) are analyzed and discussed with attention to the distortion of square-planar geometry about the Pt(II) atoms and trans-influence. These data are compared and discussed with those of Pt(η^3-$P^1N^1N^2$)(Y), Pt(η^3-$P^1N^1X^1$)(Y), (X^1=O^1, C^1, S^1, Se^1), Pt(η^3-$N^1P^1N^2$)(Cl), Pt(η^3-$S^1P^1S^2$)(Cl), Pt(η^3-$P^1S^1Cl^1$)(Cl), and Pt(η^3-$P^1Si^1N^1$)(OL) types. Each heterotridentate ligand creates two metallocyclic rings with a common central ligating atom. These η^3-ligands form twenty-three types of metallocycles and differ by the number and type of the atoms involved in the metallocyclic rings.

Keywords: structure; heterotridentate; organomonophosphines; Pt(II); distortion

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1. Introduction

Platinum compounds have significantly established themselves in the areas of biochemistry [1], catalysis [2–5], spectroscopy [6,7], and coordination theory. Very recently, a valuable review focused on the importance and advances in synthetic, structural, thermodynamic, electronic, and photophysical properties of Pt-based heteropolynuclear complexes was published [8].

Organophosphines, a soft P-donor ligand are very useful for building a wide variety of platinum complexes. We classified and analyzed structural data of monomeric platinum(II) coordination complexes with an inner coordination sphere: PtP_4, PtP_3X (X = H, F, O, N, Cl, S, Br, or I), and $PtP_{2\times2}$ (X = H, F, O, N, CN or B) in which P-donor ligands are monodentate organomonophosphines [9]. Recently, we classified and analyzed structural data of monomeric heterotridentate organomonophosphines with inner coordination spheres, Pt(η^3-$P^1N^1N^2$)(Y) (Y = CH_3 or Cl), Pt(η^3-$P^1N^1X^1$)(Y) (X^1 = O^1, Y = P^2L, Cl or I), (X^1 = C^1, Y = N^3L, Cl or Br); (X^1 = S^1; Y = Cl), and (X^1 = Se^1, Y = Cl) [10]. A very recent paper analyzed and classified X-ray data of homotridentate ligands of the Pt(η^3-$X^1X^2X^3$)(PR_3), (X = N^1, N^2, N^3; S^1, S^2, S^3; or Te^1, Te^2, Te^3) [11]. These structural studies were based on the analysis of crystallographic data. Among many other analysis methods (IR, TGA, etc.), another powerful approach for structural studies of complexes and confirming their conformations is DTF (density functional theory) as a quantum-mechanical atomistic simulation method, demonstrating recently, e.g., in refs. [12,13].

This survey aims to classify and analyze structural parameters of another class of organophoshine structures, namely Pt(η^3-$P^1C^1C^2$)(Y) (Y = NL, or I) and Pt(η^3-$P^1C^1N^1$)(Y), (Y = OL, NL, Cl or Br). The data are discussed and compared with Pt(η^3-$P^1N^1N^2$)(Y) and Pt (η^3-$P^1N^1X^1$)(Y) structures. This structural study was based on the analysis of crystallographic data that were available, unlike other methods of structural analysis, for all complexes involved in this work.

2. Results and Discussion

2.1. Pt(η^3-$P^1C^1C^2$)(Y) Type

There are five examples of Pt(η^3-$P^1C^1C^2$)(Y) type, and their structural data are gathered in Table 1. In four of them: orthorhombic [Pt{η^3-$Bu^t{}_2P(C_{18}H_{13})$}(py)] (at 110 K), and three monoclinic [Pt{η^3-$Bu^t{}_2P(C_{18}H_{13}O)$}($NCCH_3$)] (at 110 K), [Pt{η^3-$Bu^t{}_2P(C_{17}H_9F_2)$}($NCCH_3$)] (at 110 K), and [Pt{η^3-$Bu^t{}_2P(C_{17}$ $H_{10}F)$}($NCCH_3$)] (at 110 K) [14] a distorted square-planar geometry about Pt is build up by η^3-$P^1C^1C^2$ ligand and monodentate N donor atom/ligand. The structure of [Pt{η^3-$Bu^t{}_2P(C_{18}H_{13})$}(py)] [14] is shown in Figure 1 as an example. Each η^3-ligand forms two five-membered metallocyclic rings with a common C^1 atom of the $P^1C_2C^1C_2C^2$ type. The mean values of the respective chelate L-Pt-L bond angles are 83.4 (±8)° (P^1-Pt-C^1) and 81.1 (±4)° (C^1-Pt-C^2). The remaining L-Pt-L bond angles open in the order (mean values): 94.5 (±2.5)° (C^2-Pt-N) < 103.0 (±8)° (P^1-Pt-N) <163. 9 (±7)° (P^1-P^1-C^2) < 171.8 (±7)° (C^1-Pt-N). The Pt-L bond distance elongates in the order (mean values): 1.977 (±4) Å (Pt-C^1, trans N) < 2.054 (±10) Å (Pt-C^2, trans to P^1) < 2.067 (±12) Å (Pt-N) < 2.327 (±11) Å (Pt-P^1).

Table 1. Structural data for Pt(η^3-$P^1C^1C^2$)(Y) derivatives.

Complex Pt(η^3-$P^1C^1C^2$)(Y)	**Crystal cl. Space gr. Z**	**a [Å] b [Å] c [Å]**	**α [°] β [°] γ [°]**	**Chromophore Chelate Rings τ_4 [b]**	**Pt-L [a] [Å]**	**L-Pt-L [a] [Å]**	**Ref.**
[Pt{(η^3-$Bu^t{}_2P(C_{18}H_{13})$}(py)] (at 110 K)	or $P2_12_12_1$ 4	11.100(0) 12.121(0) 19.413(1)		Pt $P^1C^1C^2N$ ($P^1C_2C^1C_2C^2$) 0.171	P^1 2.328(1) $C^{1\cdot}$1.973(3) C^2 2.045(3) pyN 2.054(2)	P^1,C^1 84.2 [c] C^1,C^2 81.2 [c] P^1,C^2 165.2 P^1,N 103.4 C^2,N 99.4 C^1,N 170.7	[14]
[Pt{η^3-$Bu^t{}_2P(C_{18}H_{13}O)$}. ($NCCH_3$)] (at 110 K)	m $P2_1/n$ 4	18.058(0) 7.318(0) 19.792(0)	112.25(0)	$PtP^1C^1C^2N$ ($P^1C_2C^1C_2C^2$) 0.181	P^1 2.335(1) $C^{1\cdot}$1.981(2) C^2 2.052(2) LN 2.081(2)	P^1,C^1 83.2 [c] C^1,C^2 81.4 [c] P^1,C^2 163.0 P^1,N 103.9 C^2,N 92.0 C^1,N 171.3	[14]
[Pt{η^3-$Bu^t{}_2P(C_{17}H_9F_2)$}. P(N=CCH_3)] (at 110 K)	m $P2_1/n$ 4	16.434(0) 8.353(0) 17.385(0)	97.56(0)	$PtP^1C^1C^2N$ ($P^1C_2C^1C_2C^2$) 0.163	P^1 2.316(2) C^1 1.973(3) C^2 2.067(2) LN 2.078(2)	P^1,C^1 83.2 [c] C^1,C^2 80.7 [c] P^1,C^2 164.0 P^1,N 101.3 C^2,N 94.6 C^1,N 172.8	[14]
[Pt{η^3-$Bu^t{}_2P(C_{17}H_{10}F)$}. ($NCCH_3$)] (at 110 K)	m $P2_1/c$ 4	17.177(0) 7.446(0) 21.247(0)	106.10(0)	$PtP^1C^1C^2N$ ($P^1C_2C^1C_2C^2$) 0.171	P^1 2.329(2) C^1 1.975(3) C^2 2.068(3) LN 2.057(2)	P^1,C^1 83.2 [c] C^1,C^2 81.3 [c] P^1,C^2 163.5 P^1,N 103.2 C^2,N 92.1 C^1,N 172.3	[14]
[Pt{η^3-$Ph_2P^1(CH_2C(Me)$=C $PPh_2(C_6H_4Ph)$}(I)] (at 100 K)	tr $P\bar{1}$ 2	9.822(1) 13.373(2) 14.254(2)	65.30(3) 78.17(3) 72.61(3)	$PtP^1C^1C^2I$ ($P^1C_2C^1PCC^2$) 0.135	P^1 2.269(1) C^1 2.010(4) C^2 2.042(4) I 2.663(1)	P^1,C^1 79.3(1) C^1,C^2 86.0(1) P^1,C^2 165.0(1) P^1,I 98.5(1) C^2,I 96.3(1) C^1,I 175.9(1)	[15]

Footer: [a]. The chemical identity of the coordinated atom/ligand is specified in these columns; [b]. The parameter τ4 specifies a degree of distortion; [c]. Five-membered metallocyclic ring.

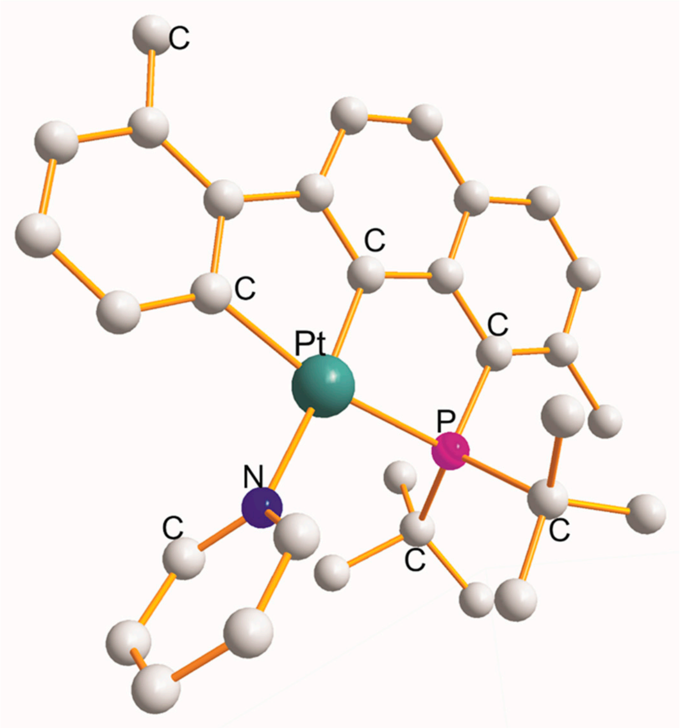

Figure 1. Structure of [Pt{η^3-$Bu^t_2P(C_{18}H_{13})$}(py) [14].

In triclinic [Pt{η^3-$Ph_2P(CH_2C(Me)=CPPh_2(C_6H_4Ph)$}(I)] (at 100K) [15], heterotridentate ligand creates two five-membered metallocyclic rings of the $P^1C_2C^1PCC^2$ type, with the values of the respective chelate L-Pt-L bond angles of 79.3° (P^1-Pt-C^1) and 86.0° (C^1-Pt-C^2). The remaining L-Pt-L bond angles open in the order: 96.3° (C^2-Pt-I) < 98.5° (P^1-Pt-I) < 165.0° (P^1-Pt-C^2) < 175.9° (C^1-Pt-I). The Pt-L bond distance elongates in the order: 2.010 Å (Pt-C^1) < 2.042 Å (Pt-C^2) < 2. 269 Å (Pt-P^1) < 2. 663 Å (Pt-I).

2.2. *Pt(η^3-$P^1C^1N^1$)(Y) Type*

There are thirteen examples of Pt(η^3-$P^1C^1N^1$)(Y) type, and their structural data are given in Table 2.

Table 2. Structural data for Pt(η^3-$P^1C^1N^1$)(Y) derivatives.

Complex **Pt(η^3-$P^1C^1N^1$)(Y)**	**Crystal cl.** **Space gr.** **Z**	**a [Å]** **b [Å]** **c [Å]**	**α [°]** **β [°]** **γ [°]**	**Chromophore** **Chelate Rings** **τ_4 [b]**	**Pt-L [a]** **[Å]**	**L-Pt-L [a]** **[Å]**	**Ref.**
[Pt{η^3-$Bu^t_2P(C_9H_9NMe_2)$}. (OH)] (at 120 k)	m $P2_1/c$ 4	20.075(4) 7.978(1) 12.800(3)	104.26(3)	$PtP^1C^1N^1O$ ($P^1C_2C^1C_3N^1$) 0.046	P^1 2.207(1) C^1 2.021(2) N^1 2.165(2) HO 2.094(2)	P^1,C^1 83.7 [c] C^2,N ^{1} 95.5 [c] P^1,N^1 175.6 P^1,O 97.3 N^1,O 83.6 C^1,O 177.8	[16]
[Pt{η^3-$Bu^t_2P(C_9H_9NMe_2)$]. (H_2O)]BF_4.thf (at 120 K)	m $P2_1/c$ 4	9.56(0) 14.941(0) 18.948(0)	97.12(0)	$PtP^1C^1N^1O$ ($P^1C_2C^1C_3N^1$) 0.094	P^1 2.233(2) C^1 1.994(3) N^1 2.166(2) H_2O 2.182(2)	P^1,C^1 84.0 [c] C^2,N ^{1} 95.9 [c] P^1,N^1 174.0 P_1O 92.7 N_1O 88.0 C_1,O 172.6	[16]
[Pt{η^3-$Bu^t_2P(C_9H_9NMe_2)$}. ($OS(=O)_2CF_3$)] (at 120 K)	or $P2_12_12_1$ 6	7.459(0) 16.565(0) 18.647(0)		$PtP^1C^1N^1O$ ($P^1C_2C^1C_3N^1$) 0.051	$P^{1.}$ 2.248(1) C^1 2.005(2) N^1 2.168(2) LO 2.249 (2)	P^1,C^1 84.6 [c] C^1,N^1 95.1 [d] P^1,N^1 174.4 P_1,O 93.9 N_1,O 86.4 C_1,O 178.2	[16]

Table 2. *Cont.*

Complex **$Pt(\eta^3\text{-}P^1C^1N^1)(Y)$**	**Crystal cl.** **Space gr.** **Z**	**a [Å]** **b [Å]** **c [Å]**	**α [°]** **β [°]** **γ [°]**	**Chromophore** **Chelate Rings** **τ_4 [b]**	**Pt-L [a]** **[Å]**	**L-Pt-L [a]** **[Å]**	**Ref.**
$[Pt\{\eta^3\text{-}Bu^t{}_2P(C_9H_9NMe_2)\}.(CO)]BF_4$ (at 120 K)	m $P2_1/c$ 4	8.554(1) 15.064(3) 12.654(4)	93.03(3)	$PtP^1C^1N^1C$ $(P^1C_2C^1C_3N^1)$ 0.105	$P^{1\cdot}$ 2.227(2) C^1 2.063(3) N^1 2.158(2) OC 1.922(3)	P^1,C^1 83.1 [c] C^2,N^1 88.9 [d] P^1,N^1 172.9 P^1,C 94.4 N^1,C 94.4 C^1,C 172.3	[16]
$[Pt\{\eta^3\text{-}Bu^t{}_2P(C_9H_9NMe_2)\}.(CH_3)]$ (at 120 K)	tg R-3 8	24.224(3) 17.904(4)		$PtP^1C^1N^1C$ $(P^1C_2C^1C_3N^1)$ 0.051	P^1 2.204(2) C^1 2.075(2) N^1 2.193(2) H_3C 2.187(2)	P^1,C^1 83.4 [c] C^1,N^1 93.4 [d] P^1N^1 177.4 P^1,C 94.0 N^1,C 89.4 C^1,C 175.2	[17]
$[Pt\{\eta^3\text{-}Bu^t{}_2P(C_9H_9NMe_2)\}\{C(Ph)=N=N)\}$ (at 120 K)	tr $P\bar{1}$ 2	9.004(1) 10.345(2) 14.201(3)	72.53(8) 88.51(3) 77.85(3)	$PtP^1C^1\ N^1C$ $(P^1C_2C^1C_3N^1)$ 0.158	P^1 2.220(1) C^1 2.053(2) N^1 2.176(2) LC 2.146(3)	P^1,C^1 83.6 [c] C^1,N^1 93.2 [d] P^1N^1 168.0 P^1,C 96.8 N^1,C 88.4 C^1,C 169.5	[18]
$[Pt\{\eta^3\text{-}Bu^t{}_2P(C_8H_7NEt_2)\}.(Cl)]$ (at 120 K)	m $P2_1/n$ 4	12.065(2) 13.391(3) 13.625(3)	104.69(3)	$PtP^1C^1N^1Cl$ $(P^1C_2C^1C_3N^1)$ 0.138	P^1 2.217(1) C^1 1.971(2) N^1 2.191(2) Cl 2.408(1)	P^1,C^1 83.6 [c] C^1,N^1 82.8 [c] P^1,N^1 166.2 P^1,Cl 100.5 N^1,Cl 93.2 C^1,Cl 174.3	[16]
$[Pt\{\eta^3\text{-}Bu^t{}_2P(C_9H_9NMe_2)\}.\ (Cl)]$ (at 120 K)	m $P2_1/c$ 4	16.431(3) 7.487(1) 17.060(3)	108.35(3)	$PtP^1C^1N^1Cl$ $(P^1C_2C^1C_2N^1)$ 0.077	P^1 2.226(1) C^1 2.020(2) N^1 2.189(2) Cl 2.419(2)	P^1,C^1 84.8 [c] C^1,N^1 94.4 [d] P^1,N^1 174.2 P^1,Cl 93.9 N^1,Cl 87.2 C^1,Cl 174.8	[17]
$[Pt\{\eta^3\text{-}Ph_2P(C_{16}H_{13}NMe_2)\}.(Cl)]$ (at 103 K)	tr $P\bar{1}$ 2	9.528(0) 10.415(0) 14.436(0)	81.31(0) 74.58(0) 66.96(0)	$PtP^1C^1N^1Cl$ $(P^1C_3C^1C_2N^1)$ 0.066	P^1 2.196(1) C^1 1.992(2) N^1 2.152(2) Cl 2.384(1)	P^1,C^1 95.5 [d] C^1,N^1 82.2 [c] P^1,N^1 176.1 P^1,Cl 89.5 N^1,Cl 92.6 C^1,Cl 174.4	[19]
$[Pt\{\eta^3\text{-}Ph_2P(C_{23}H_{28}N_3)\}.(Cl)]PF_6.thf$	tg 14 8	21.495(0) 19.249 (0)		$PtP^1C^1N^1Cl$ $(P^1C_3NC^1NC_3N^1)$ 0.074	P^1 2.258(1) C^1 1.991(2) N^1 2.073(3) Cl 2.347(1)	P^1,C^1 92.8 [e] C^1,N^1 86.1 [e] P^1,N^1 178.2 P^1,Cl 93.8 N^1,Cl 87.1 C^1,Cl 171.3	[20]
$[Pt\{\eta^3\text{-}Ph_2P(C_8H_6O_2NPh)\}.(NCCH_3)]BF_4$ (at 110 K)	m $P2_1/c$ 4	15.601(0) 9.496(0) 21.046(0)	120.60(0)	$PtP^1C^1N^1N$ $(P^1OCC^1C_2N^1)$ 0.186	P^1 2.200(2) C^1 1.950(1) N^1 2.127(2) N 2.066(2)	P^1,C^1 80.3 [c] C^1,N^1 79.4 [c] P^1,N^1 159.2 P^1,N 104.1 N^1,N 96.3 C^1,N^1 174.4	[21]
$[Pt\{\eta^3\text{-}Ph_2P(C_8H_6O_2NPh)\}.(Br)]$ (at 150 K)	or $P2_12_12_1$ 6	14.459(0) 14.757(0) 21.590(0)		$PtP^1C^1N^1Br$ $(P^1OCC^1C_2N^1)$ 0.156	P^1 2.177(2) C^1 1.946(3) N^1 2.134(3) Br 2.488(1)	P^1,C^1 81.0 [c] C^1,N^1 79.0 [c] P^1,N^1 159.9 P^1,Br 100.9 N^1,Br 99.1 C^1,Br 178.1	[21]
$[Pt\{\eta^3\text{-}Pr^i{}_2P(C_{11}H_{15}NO_2)\}.\ (Br)]$ (at 150 K)	or $Pna2_1$ 6	23.138(0) 10.031(0) 8.207(0)		$PtP^1C^1N^1Br$ $(P^1OCC^1C_2N^1)$ 0.176	P^1 2.180(1) C^1 1.966(6) N^1 2.192(5) Br 2.509(2)	P^1,C^1 82.1(2) [c] C^1,N^1 79.9(2) [c] P^1,N^1 159.4(1) P^1,Br 99.8(1) N^1,Br 97.5(1) C^1,Br 175.8(1)	[22]

Footer: [a]. The chemical identity of the coordinated atom/ligand is specified in these columns; [b]. The parameter τ4 specifies a degree of distortion; [c]. Five-membered metallocyclic ring; [d]. Six-membered metallocyclic ring; [e]. Seven-membered metallocyclic ring.

2.2.1. Pt(η^3-$P^1C^1N^1$)(OL) Type

In three complexes, two monoclinic [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}(OH)] (at 120 K), [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}(H_2O)]BF_4.thf (at 120 K) and orthorhombic [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}($OS(=O)_2CF_3$)] (at 120 K) [16] a distorted square planar geometry about Pt(II) atom is built up by η^3-$P^1C^1N^1$ ligand and monodentate OL. Each heterotridentate ligand creates two metallocyclic rings, each one five- and six-membered with common C^1 atom of the type $P^1C_2C^1C_3N^1$ with the mean values of the respective chelate L-Pt-L bond angles of 84.1 (±4)° (P^1-Pt-C^1) and 95.5 (±4)° (C^1-Pt-N^1). The remaining L-Pt-L bond angles open in the order (mean values): 86.0 (±1.2)° (N^1-Pt-O) < 94.6 (±1.6)° (P^1-Pt-O) < 174.6 (±7)° (P1-Pt-N^1) < 175.9 (±2.7)° (C^1-Pt-O). The Pt-L bond distance elongates in the order (mean values): 2.007 (± 13] Å (Pt-C^1, trans to O) < 2.166 (±2) Å (Pt-N^1, trans to P^1) < 2.175 (±5) Å (Pt-O) < 2.229 (±19) (Pt-P^1).

2.2.2. Pt ($\eta^{3-}P^1C^1N^1$)(CL) Type

In another three complexes, monoclinic [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}(CO)]BF_4 (at 120 K) [15], tetragonal [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}(CH_3)] (at 120 K) [17], and triclinic [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}{C(Ph)=N=N}] (at 120 K) [17] the η^3-$P^1C^1N^1$ ligand with monodentate C-donor ligand completed a distorted square planar geometry ($PtP^1C^1N^1C$). The heterotridentate ligand created five- and six-membered metallocyclic rings with a common C^1 atom of the $P^1C_2C^1C_3N^1$ type. The mean values of the respective chelate L-Pt-L bond angles are 83.4 (±4)° (P^1-Pt-C^1) and 91.8 (±2.5)° (C^1-Pt-N^1). The remaining L-Pt-L bond angles open in the order (mean values): 90.7 (±3.7)° (N^1-Pt-C) < 94.9 (±1.9) (P^1-Pt-C) < 171.8 (±3.8)° (P^1-Pt-N^1) < 172.3 (±2.8)° (C^1-Pt-C). The Pt-L bond distance elongates in the order (mean values): 2.064 (±9) Å Pt-C^1, trans to C) < 2.080 (±16) Å (Pt-C) < 2.175 (±12) Å (Pt-N^1, trans to P^1) < 2.232 (±25) Å (Pt-P^1).

2.2.3. Pt(η^3-$P^1C^1N^1$)(Cl) Type

There are four complexes of this type. In monoclinic [Pt{η^3-$Bu^t{}_2P(C_8H_7NEt_2)$}(Cl)] (at 120 K) [16] the η^3-ligand creates two five-membered metallocyclic rings with common C^1 atom of the $P^1C_2C^1C_2N^1$ type. The values of the respective chelate L-Pt-L bond angles are 83.6° (P^1-Pt-C^1) and 82.8° (C^1-Pt-N^1). The remaining angles are 97.2° (N^1-Pt-Cl), 100.5° (P^1-Pt-Cl), 166.2° (P^1-Pt-N^1), and 174.3° (C^1-Pt-Cl).

In another monoclinic [Pt{η^3-$Bu^t{}_2P(C_9H_9NMe_2)$}(Cl)] (at 120 K) [17], heterotridentate ligand creates five- and six-membered metallocyclic rings with common C^1 atom of the $P^1C_2C^1C_3$ N^1 type. The values of the respective L-Pt-L bond angles are 84.8° (P^1-Pt-C^1) and 94.4° (C^1-Pt-N^1). The values for remaining L-PL-L bond angles open in the order: 87.2° (N^1-Pt-Cl) < 93.9° (P^1-Pt-Cl) < 174.2° (P^1-Pt-N^1) < 174.8° (C^1-Pt-Cl).

In triclinic [Pt{η^3-$Ph_2P(C_{16}H_{13}NMe_2)$}(Cl)] (at 103 K) [19] the η^3-ligand forms $P^1C_3C^1C_2$ N^1 type with the values of L-Pt-L chelate angles of 95.9° (P^1-Pt-C^1) and 82.2° (C^1-Pt-N^1). The remaining L-Pt-L bond angles open in the order: 89.5° (P^1-Pt-Cl) < 92.6° (N^1-Pt-Cl) < 174.4° (C^1-Pt-Cl) < 176.1° (P^1-Pt-N^1).

The $P^1C_3NC^1NC_3N^1$ type was formed in tetragonal [Pt{η^3-$Ph_2P(C_{23}H_{28}N_3)$}(Cl)]PF_6.thf Figure 2 [20]. The values of chelate L-Pt-L angles are 92.8° (P^1-Pt-C^1) and 86.1° (C^1-Pt-N^1). The remaining L-Pt-L bond angles open in the order 87.1° (N^1-Pt-Cl) < 93.8° (P^1-Pt-Cl) < 171.3° (C^1-Pt-Cl) < 178.2° (P^1-Pt-N^1).

The Cl^- completed a distorted square planar geometry in these complexes about each Pt(II) atom. The Pt-L bond distance elongates in the order (mean values): 1.994 (±26) Å (Pt-C^1, trans to Cl) < 2.151 (±25) Å (Pt-N^1), trans to P^1) < 2.223 (±15) Å (Pt-P^1) < 2.389 (±72) Å (Pt-Cl).

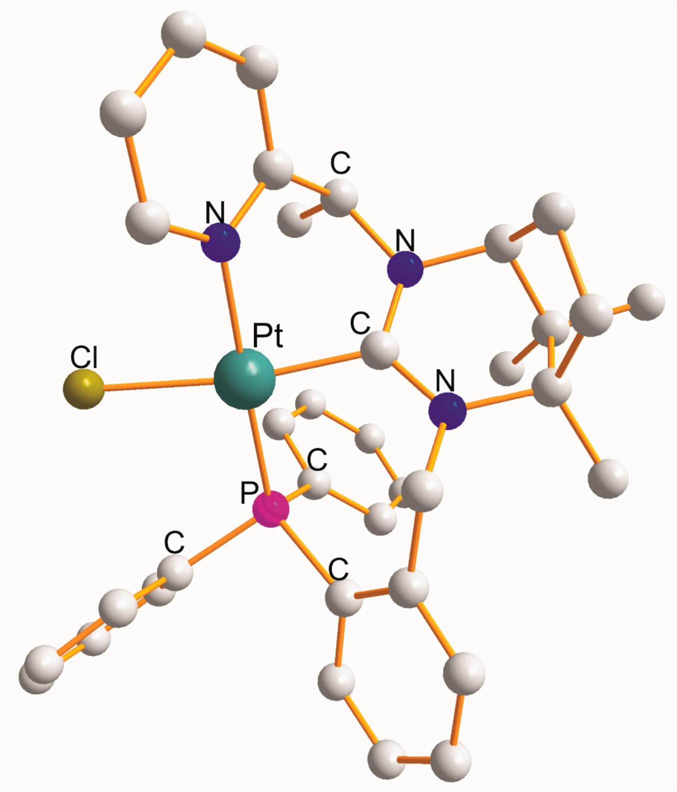

Figure 2. Structure of [Pt{η^3-$Ph_2P(C_{23}H_{28}N_3)$}(Cl)] [20].

2.2.4. Pt(η^3-$P^1C^1N^1$)(Y) (Y = NL, Br) Type

Monoclinic [Pt{η^3-$Ph_2P(C_8H_6O_2NPh)$}($NCCH_3$)]BF_4 (at 110 K) [21] is the only example in which a η^3-ligand with monodentate $NCCH_3$ ligand built up a distorted square planar geometry about Pt(II) atom. The heterotridentate ligand creates two five-membered metallocyclic rings of the $P^1OCC^1C_2N^1$ type. The values of the respective chelate L-PL-L bond angles are 80.3° (P^1-Pt-C^1), and 79.4° (C^1-Pt-N^1). The remaining L-Pt-L bond angles open in the order: 96.3° (N^1-Pt-N) < 104.1° (P^1-Pt-N) < 159.2° (P^1-Pt-N^1) < 174.4° (C^1-Pt-N). The Pt-L bond distance elongates in the order: 1.950 Å (Pt-C^1, trans to N) < 2.066 Å (Pt-N) < 2.127 Å (Pt-N^1) < 2.200 Å (Pt-P^1, trans to N^1).

In two orthorhombic [Pt{η^3-$Ph_2P(C_8H_6O_2NPh)$}(Br)] (at 150 K) [21] and [Pt{η^3-$Pr^i_2P(C_{11}H_{15}NO_2)$}(Br)] (at 150 K) [22], each η^3-ligand creates two five-membered metallocyclic rings with common C^1 atom of the $P^1OCC^1C_2N^1$ type. The values of the respective chelate L-Pt-L bond angles (mean values) are 81.6° (P^1-Pt-C^1) and 79.5° (C^1-Pt-N^1). The remaining L-Pt-L bond angle open in the order (mean values): 98.3° (N^1-Pt-Br) < 100.3° (P^1-Pt-Br) < 159.6° (P^1-Pt-N^1) < 176.9° (C^1-Pt-Br). The Pt-L bond distance elongates in the order (mean values): 1.956 Å (Pt-C^1) < 2.163 Å (Pt-N^1) < 2.179 Å (Pt-P^1) < 2. 498 Å (Pt-Br).

3. Conclusions

This paper includes eighteen monomeric Pt(II) complexes with compositions Pt(η^3-$P^1C^1C^2$)(Y) (Y = NL, or I) and Pt(η^3-$P^1C^1N^1$)(Y), (Y = OL, NL, CL, Cl or Br). Recently, we classified and analyzed structural parameters of Pt(η^3-$P^1N^1N^2$)(Y), (Y = CL or Cl); Pt(η^3-$P^1N^1O^1$)(Y), (Y = PL, Cl or I); Pt(η^3-$P^1N^1C^1$)(Y), (Y = NL or Cl); Pt(η^3-$P^1N^1S^1$)(Y), (Y = Cl or I); Pt(η^3-$P^1N^1Si^1$)(Cl); Pt(η^3-$N^1P^1N^2$)(Cl); Pt(η^3–$S^1P^1S^2$)(Cl); Pt(η^3-$P^1S^1Cl^1$)(Cl) and Pt(η^3-$P^1Si^1N^1$)(OL) [10].

Each heterotridentate ligand creates two metallocyclic rings. These eleven sub-groups of η^3-ligands build up twenty-three metallocycles types. These types based on the membered number of atoms in the chelate L-Pt-L angles with mean values are:

5+5: $P^1C_2C^1C_2C^2$, $P^1C_2C^1PCC^2$, $P^1C_2C^1C_2N^1$, $P^2OCC^1C_2N^1$, $P^1C_2N^1C_2N^2$, $P^1C_2N^1NCO^1$, $P^1C_2N^1NCC^1$, $S^1C_2P^1C_2S^2$; Σ 84.6/82.6°

5+6: $P^1C_2C^1C_3N^1$, $P^1C_2N^1C_3O^1$, $P^1C_2S^1C_2BCl^1$, $P^1C_2Si^1C_3N^1$; Σ 85.5/92.9°

6+5: $P^1C_3C^1C_2N^1$, $P^1C_3N^1C_2N^2$, $P^1C_3N^1NCN^2$, $P^1C_3N^1C_2C^1$, $P^1C_3N^1NCS^1$; Σ 94.4/83.8°

6+6: $P^1C_3N^1C_3N^2$, $P^1C_3N^1C_3O^1$, $P^1C_3N^1C_3S^1$, $P^1C_3N^1C_3Se^1$; Σ 91.1/91.7°

7+7: $P^1C_3NC^1NC_3N^1$; Σ 92.8/86.1°

There are at least two contributing factors to the size of the chelate bond angles both ligands based. One is the steric constraints imposed on the ligand and the other is the need to accommodate tridenticity where appropriate.

The Pt-P^1 (trans to X^1) bond distance elongates in the sequence (total mean values): 2.198 Å (X = Cl) < 2.206 Å (N^2) < 2. 211 Å (O^1) < 2. 215 Å (N^1) < 2.239 Å (S^1) < 2.260 Å (C^1) < 2.327 Å (CL) < 2.407 Å (Se^1).

The Pt-Y (trans to X^1) bond distances elongate in the sequences: (total mean values):

Pt-NL: 2.02 Å (N^1) < 2.097 Å (C^1); Pt-OL: 2.175 Å (C^1) < 2.353 Å (Si^1);

Pt-CL: 2.068 Å (N^1) < 2.085 Å (C^1); Pt-Cl: 2.332 Å (N^1) < 2.372 Å (P^1) < 2.380 Å (S^1) < 2.389 Å (C^1); Pt-PL: 2.265 Å (N^1); Pt-Br: 2.490 Å (C^1); Pt-I: 2.590 Å (N^1) < 2.663 Å (C^1). These values correspond quite well with the trans influence of the respective X^1-donor atoms.

In transition metal complexes, the oxidation state plays a leading role in the geometry formed and platinum is no exception. In four coordinate Pt(II) prefers a square planar geometry. The utility of a simple metric to assess molecule shape and degree of distortion best exemplified the τ_4 parameter via an equation introduced by [23]:

$\tau_4 = \frac{360-(\alpha+\beta)}{141}$ where β and α are the two largest angles and assume the value of 0 and 1 for the perfect square planar and perfect tetrahedral geometries, respectively.

The total mean values of τ_4 and some structural parameters for the respective metallocycles are gathered in the following summary in Table 3:

Table 3. Summary of total mean values of τ_4 and selected structure parameters of analyzed metallocycles.

Chelate Rings Membered	Σ Sums of Chelate Rings L-Pt-L/L-Pt-L°	trans α L-Pt-L°	trans β L-Pt-L°	Σ trans $\alpha+\beta$ L-Pt-L°	τ_4
5+5	167.4	163.3	174.4	337.7	0.158
5+6	176.3	172.3	174.4	346.8	0.094
6+5	177.8	175.2	173.8	349.0	0.079
7+7	178.9	178.2	171.3	349.5	0.074
6+6	183.7	176.5	175.5	352.0	0.056

It is well known that a distortion of a square-planar geometry around a metal atom diminishes with opening trans-L-Pt-L angles. As can be seen, the membered of metallocycles also play a role. When the sums of a "pair" of the respective L-Pt-L chelate, the angles distortion decreases.

We believe that such a structural analysis can continue to serve a useful function by centralizing available material in a wide scale of Pt complexes and delineating areas worthy of further investigation.

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Abbreviations

$Bu^t{}_2P(C_8H_7NEt_2)$	(2-((di-t-butylphosphino)methyl)-6-((diethylamino)methyl) phenyl)
$Bu^t{}_2P(C_{18}H_{13}O)$	(8-(di-t-butylphosphanyl)-7-methy-2-(4-methoxybenzene-1,2-diyl) naphthalene-1-yl)
$Bu^t{}_2P(C_{17}H_{10}F)$	(8-(di-t-butylphosphanyl)-7-methyl-2-(4-fluorobenzene-1,2-diyl) naphthalene-1-yl)
$Bu^t{}_2P(C_{17}H_9F_2)$	(8-(di-t-butylphosphanyl)-7-methyl-2-(3,5-difluorobenzene-1,2-diyl) naphthalene-1-yl)
$Bu^t{}_2P(C_{18}H_{13})$	(8-(di-t-butylphosphanyl)-7-methyl-2-(6-methylbenzen-1,2-yl) naphthalen-1-yl)
$Bu^t{}_2P(C_9H_9NMe_2)$	(2-dimethylamino)ethyl)-6-2-(di-t-butylphosphinomethyl)-6-phenyl)
m	monoclinic
or	orthorhombic
$Ph_2P(C_{16}H_{13}NMe_2)$	(2-(1-(dimethylamino)ethyl)-6-(2-diphenylphosphino)-2-phenylvinyl)phenyl)
$Ph_2P(C_{23}H_{28}N_3)$	(2-(2-(diphenylphoshino)benzyl)-1,8,8-trimethyl-4-(1-(pyridine-2-yl)ethyl)-2,4-diazobicyclo [9.2.1] octan-3-ylidene)
$Ph_2P(C_8H_6O_2NPh)$	(2-((diphenylphosphino)oxy)-3-methoxy-6-(phenylimino) methyl)phenyl)
$Ph_2P(CH_2C(Me)=C$	(3-(2-(2-methyl-3-diphenylphosphinopropenyl)
$Ph_2P(C_6H_4Ph)$	diphenylphosphino)biphenyl
$Pr^i{}_2P(C_7H_5ONC_4H_8 0)$	(2-((di-isopropylphosphino)oxy)-6-morpholino-4-yl)methyl)phenyl)
py	pyridine
tg	tetragonal
tr	triclinic
$Te^{1,2,3}$	represents ligating Te atoms differing in distances/angles with Pt atoms
$P^1C_2C^1C_2C^2$ (and sim.)	superscripts represent the ligating donor atoms, in case of the same atoms they are differing in distances/angles with Pt atoms; subscripts represent atoms which are located between the respective donor atoms
NL, OL, CL	N-donor ligand, O-donor ligand, C-donor ligand, respectively

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