



Review Heterotridentate Organomonophosphines in $Pt(\kappa^3 - X^1P^1X^2)(Y)$ $(X^{1,2} = N^{1,2} \text{ or } S^{1,2})$, $Pt(\kappa^3 - P^1N^1X^1)(Y)$ $(X^1 = O, C, S \text{ or } Se)$ $Pt(\kappa^3 - P^1S^1Cl^1)(Cl)$ and $Pt(\kappa^3 - P^1Si^1N^1)(OL)$ —Structural Aspects

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Abstract: This review covers twenty four Pt(II) complexes of the inner coordination sphere Pt(κ^{3} –P¹ N¹N²)(Y), (Y = Cl, CL); Pt(κ^{3} –P¹N¹X¹)(Y), (X¹ = O¹ and Y = P²L, Cl, I); (X¹ = C¹ and Y = NL, Cl); (X¹ = S¹ and Y = Cl, I); (X¹ = Se¹ and Y = Cl); Pt(κ^{3} –N¹P¹N²)(Cl), Pt(κ^{3} –S¹P¹S²)(Cl), Pt(κ^{3} –P¹S¹Cl¹)(Cl) and Pt(κ^{3} –P¹Si¹N¹)(OL). These complexes are crystallized in three crystal classes: monoclinic (16 examples), triclinic (5 examples), and orthorhombic (3 examples). Each κ^{3} –ligand creates two metallocyclic rings with various combinations of the respective metallocyclic rings. If the common central ligating atom is N¹, the 5 + 5 membered, 5 + 5, 5 + 6, 6 + 5, and 6 + 6; if the common central ligating atom is P¹: 5 + 5, and 6 + 6; if the common central ligating atom is S¹ or Si¹, 5 + 6-membered. The structural parameters (Pt-L, L-Pt-L) are analysed and discussed with an attention to the distortion of a square-planar geometry about the Pt(II) atoms as well as trans-influence. The sums of the Pt-L (x = 4) bond distances the growing with the covalent radius of the Y atoms. Noticeably, the distortion of the square-planar geometry is growing with the decreasing size of the inner coordination sphere about the Pt(II) atom. There is a relation between the degree of distortion (T 4) and the numbers of the metallocycles rings. The distortion diminishing is in the order of: 0.058 (5 + 5) > 0.037 (6 + 5) > 0.023 (5 + 6) > 0.022 (6 + 6) membered.

Keywords: structure; $Pt(\kappa^3 - P^1X^1X^2)(Y)$; $Pt(\kappa^3 - X^1P^1X^2)(Y)$; distortion; *trans*-influence

1. Introduction

Platinum exists in a wide range of oxidation states from zero to +6, including nonintegral, Pt(2.25), Pt(2.81), Pt(3.25) and Pt(3.5). Of these, particularly in four- and sixcoordinated, +2 and +4 oxidation states are the most common. The many platinum coordination complexes have been surveyed [1–3], converting the crystallographic and structural data of almost two thousand monomeric examples.

About 10% of these complexes exist as isomers. Their structural data were analysed and classified [4]. Included are distortion (65%) *cis-trans* (30%), mixed isomers (*cis-trans* and distortion) and ligand isomers. Despite the importance of *cis-trans* geometry in the chemistry of Pt(II), the distortion isomers atom is far more common.

Recently, we detail analysed the structural data of distortion isomers of the *cis*-Pt(II) complexes, and none of the *cis*-isomer has a *trans*-partner. The distortion isomers differ mostly in Pt-L distances as well as the values of the L-Pt-L angles [5]. Another review has focused on the ligand isomers of Pt(II) complex [6].

Organomonophosphines as a soft P-donor ligand are very useful for building a wide variety of platinum complexes. Research activity in this field is always very active. Organophosphines on the basis of donor atoms can be divided into four sub-groups:



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). homodentate (P, PP, PPP, PPPP), heterobi- (PO, PN, PB, PS) and heterotridentate (POP, PNP, PCP, PBP, PSP, PSiP) as well as tetradentate (P₄, P₃Si, P₂N₂, P₂S₂, P₂C₂, PN₃) [7–9].

The aim of this survey is to correlate the structural parameters available for heterotridentate organomonophosphines of the types: $Pt(\kappa^3-P^1N^1X^1)(Y)$ (X = N², O¹, C¹, S¹, Se¹), $Pt(\kappa^3-N^1P^1N^2)(Cl)$, $Pt(\kappa^3-S^1P^1S^2)(Cl)$, $Pt(\kappa^3-P^1S^1Cl^1)(Y)$ and $Pt(\kappa^3-P^1Si^1N^1)(OL)$.

2. Results and Discussion

2.1. $Pt(\kappa^3 - P^1N^1N^2)(Y)$ Derivatives

There are nine examples of the Pt(κ^3 –P¹N¹N²)(Y) type, and their structural parameters are gathered in Table 1 (A: Pt(κ^3 -P¹N¹N²)(Y)). In triclinic [Pt{ κ^3 –Bu^t₂P¹(CH₂)(C₅H₃N¹) (CH₂)N²Et₂}(Cl)].C₆H₆ (at 120 K) [10], heterotridentate κ^3 –P¹N¹N² ligand creates two five-membered metallocyclic rings with the central common ligating N¹ atom of P¹C₂N¹C₂N² type with the values of the respective rings of 85.5° (P¹-Pt-N¹) and 83.4° (N¹-Pt-N²). The Cl⁻ completed a square-planar geometry about Pt(II) atom. The remaining L-Pt-L bond angles open in the sequence 92.6° (N²–Pt–Cl) < 98.5° (P¹–Pt–Cl) < 168.0° (P¹–Pt–N²) < 176.0° (N¹–Pt–Cl). The Pt-L bond distance elongates in the order: 1.997 Å (Pt–N¹ trans to Cl) < 2.149 Å (Pt–N² trans to P¹) < 2.236 Å (Pt–P¹) < 2.296 Å (Pt–Cl).

Table 1. Structural data for $Pt(\kappa^3-P^1N^1N^2)(Y)$ and $Pt(\kappa^3-P^1N^1X^1)(Y)$ ($X^1 = O^1$, C^1 , S^1 or Se^1), ($Y = variable monodentate atoms/ligands)^a$.

Complex	Space gr. Cryst. cl. Z	a [Å] b [Å] c [Å]	α[°] β[°] γ[°]	Chromophore (Chelate Rings) T_4^{b}	Pt-L ^c [Å]	L-Pt-L ^c [°]	Ref. REFCODE
A: $Pt(\kappa^3 - P^1N^1N^2)(Y)$							
$\begin{array}{c} [Pt[\kappa^3\text{-}Bu^t_2P(CH_2)(C_5H_3N^1).\\ (CH_2)N^2E_{12}](C)].C_6H_6\\ (at\ 120\ K) \end{array}$	tr Pī 2	9.158(0) 10.963(0) 16.018(0)	77.29(0) 76.97(0) 69.11(0)	$PtP^1N^1N^2Cl$ $P^1C_2N^1C_2N^2$ 0.044	P ¹ 2.236(1) N ¹ 1.997(2) N ² 2.149(2) Cl 2.296(2)	P ¹ ,N ¹ 85.5 ^d N ¹ ,N ² 83.4 ^d P ¹ ,N ² 168.0 P ¹ ,Cl 98.5 N ² ,Cl 92.6 N ¹ ,Cl 176.0	[10] WOGDAY
$\begin{array}{c} [Pt \{\kappa^{3} \text{-} Ph_{2} P^{1} (C_{7} H_{5} N^{1}). \\ (C_{2} H_{2} O) N^{2} C_{6} H_{4} OH)] (CH_{3})]. \\ (CHCl_{3}) \\ (at 150 \text{ K}) \end{array}$	tr Pī 2	9.917(1) 11.944(2) 14.872(2)	99.17(0) 103.82(0) 112.53(0)	${}^{PtP^1N^1N^2C}_{P^1C_3N^1C_2N^2}_{0.032}$	$\begin{array}{c} P^1 \ 2.179(1) \\ N^1 \ 2.050(2) \\ N^2 \ 2.089(2) \\ H_3C \ 2.045(2) \end{array}$	P ¹ ,N ¹ 95.3 ^e N ¹ ,N ² 80.5 ^d P ¹ ,N ² 173.7 P ¹ ,C 89.0 N ² ,C 95.5 N ¹ ,C 174.7	[11] GAJMOV
$\begin{array}{c} [Pt [\kappa^3 \mbox{-}Ph_2 P^1 (C_7 H_5 N^1). \\ (C_2 H_2 O) N^2 (C_6 H_4 OH)] (CH_3)]. \\ 1.5 \mbox{ toluene} \\ (at 150 \mbox{ K}) \end{array}$	m P2 ₁ /c 4	11.882(1) 14.184(1) 21.892(1)	103.75(0)	${}^{PtP^1N^1N^2C}_{P^1C_3N^1C_2N^2}_{0.027}_{0.027}$	$\begin{array}{c} P^1 \ 2.184(2) \\ N^1 \ 2.061(3) \\ N^2 \ 2.075(3) \\ H_3C \ 2.051(2) \end{array}$	P ¹ ,N ¹ 95.4 ^e N ¹ ,N ² 81.0 ^d P ¹ ,N ² 176.4 P ¹ ,C 90.5 N ² ,C 93.0 N ¹ ,C 174.0	[11] GAJMUB
$\begin{array}{c} [Pt\{\kappa^{3}\text{-}Ph_{2}P^{1}(C_{7}H_{5}N^{1}).\\ (C_{3}H_{6})N^{2}(C_{7}H_{5}O_{2})](CH_{3})].\\ 2 \text{ toluene}\\ (at 150 \text{ K}) \end{array}$	m P2 ₁ /c 4	14.859(0) 15.607(0) 16.287(0)	95.88(0)	$\begin{array}{c} PtP^{1}N^{1}N^{2}C\\P^{1}C_{3}N^{1}C_{2}N^{2}\\0.033\end{array}$	$\begin{array}{c} P^1 \ 2.189(1) \\ N^1 \ 2.077(2) \\ N^2 \ 2.070(2) \\ H_3C \ 2.062(2) \end{array}$	P ¹ ,N ¹ 95.2 ^e N ¹ ,N ² 80.3 ^d P ¹ ,N ² 175.4 P ¹ ,C 89.4 N ² ,C 94.9 N ¹ ,C 172.6	[11] GAJNAI
$\begin{array}{c} [Pt[\kappa^{3}\text{-}Ph_{9}P^{1}(C_{7}H_{5}N^{1})(C_{6}H_{4})N^{2}\\ (C_{10}H_{9}NO_{3})](CH_{3})]Et_{2}O\\ (at\ 150\ K) \end{array}$	m P2 ₁ /c 4	10.992(0) 20.133(0) 16.933(0)	101.72(0)	${}^{PtP^1N^1N^2C}_{P^1C_3N^1C_2N^2}_{0.040}_{0.040}$	$\begin{array}{c} P^1 \ 2.184(1) \\ N^1 \ 2.087(2) \\ N^2 \ 2.086(2) \\ H_3C \ 2.062(2) \end{array}$	P ¹ ,N ¹ 92.6 ^e N ¹ ,N ² 79.4 ^d P ¹ ,N ² 171.8 P ¹ ,C 91.5 N ² ,C 96.6 N ¹ ,C 173.7	[12] QICYAD
$\begin{array}{c} [Pt[\kappa^{3}\text{-}Ph_{2}P^{1}(C_{7}H_{5}N^{1})(C_{5}H_{7}O)\\ N^{2}(C_{10}H_{10}N_{2})](CH_{3})]H_{2}O\\ (at~93~K) \end{array}$	${{\rm P2}_1/c} {4}$	8.739 (1) 14.988(2) 25.469(2)	94.23(0)	$PtP^1N^1N^2C$ $P^1C_3N^1C_2N^2$ 0.052	$\begin{array}{c} P^1 \ 2.190(1) \\ N^1 \ 2.061(2) \\ N^2 \ 2.094(2) \\ H_3C \ 2.083(2) \end{array}$	P ¹ ,N ¹ 89.4 ^e N ¹ ,N ² 79.6 ^d P ¹ ,N ² 169.0 P ¹ ,C 92.2 N ² ,C 93.7 N ¹ ,C 172.1	[13] DIYYIU
$[Pt] \kappa^{3}-Ph_{2}P^{1}(C_{7}H_{5}N^{1})(C_{2}H_{2}O) \\ N^{2}(C_{6}H_{4}OH)(CH_{3})]CHCl_{3} \\ (at 150 \text{ K})$	m P2 ₁ /c 4	10.191(0) 16.863(1) 17.525(1)	97.30(0)	${}^{PtP^1N^1N^2C}_{P^1C_3N^1C_2N^2}_{0.030}$	$\begin{array}{c} P^1 \ 2.183(1) \\ N^1 \ 2.059(1) \\ N^2 \ 2.061(1) \\ H_3C \ 2.055(1) \end{array}$	$\begin{array}{c} P^{1}, N^{1} \ 95.1 \ ^{e} \\ N^{1}, N^{2} \ 81.0 \ ^{d} \\ P^{1}, N^{2} \ 175.8 \\ P^{1}, C \ 91.2 \\ N^{2}, C \ 92.6 \\ N^{1}, C \ 173.4 \end{array}$	[14] CAJLAC

Complex

Space gr. Cryst. cl. Z	a [Å] b [Å] c [Å]	α[°] β[°] γ[°]	Chromophore (Chelate Rings) T4 ^b	Pt-L ^c [Å]	L-Pt-L ^c [°]	Ref. REFCODE
tr Pī 2	7.431(2) 10.031(3) 14.797(5)	101.10(0) 95.70(0) 98.76(0)	$\begin{array}{c} PtP^{1}N^{1}N^{2}C\\P^{1}C_{3}N^{1}NCN^{2}\\0.038\end{array}$	$\begin{array}{c} P^1 \; 2.219(1) \\ N^1 \; 2.164(2) \\ N^2 \; 2.050(1) \\ Cl \; 2.297(2) \end{array}$	P ¹ ,N ¹ 95.8 ^e N ¹ ,N ² 79.3 ^d P ¹ ,N ² 173.0 P ¹ ,Cl 90.8 N ² ,Cl 94.2 N ¹ ,Cl 173.4	[15] XUYWEU
m P2 ₁ /c 4	18.910(3) 10.098(1) 19.429(3)	118.93(1)	PtP ¹ N ¹ N ² Cl P ¹ C ₃ N ¹ CN ² 0.020	$\begin{array}{c} P^1 \; 2.234(1) \\ N^1 \; 2.120(1) \\ N^2 \; 2.104(1) \\ Cl \; 2.284(1) \end{array}$	P ¹ ,N ¹ 93.3 ^e N ¹ ,N ² 85.6 ^d P ¹ ,N ² 178.7 P ¹ ,Cl 91.8 N ² ,Cl 89.2 N ¹ ,Cl 174.0	[16] IFUQEF
tr Pī 2	12.614(2) 13.671(2) 15.754(3)	100.26(0) 99.33(0) 110.68(0)	PtP ¹ N ¹ O ¹ P P ¹ C ₂ N ¹ NCO ¹ 0.067	P ¹ 2.233(2) N ¹ 1.985(2) O ¹ 2.050(2) LP 2.261(1)	P ¹ ,N ¹ 83.6 ^d N ¹ ,O ¹ 78.8 ^d P ¹ ,O ¹ 162.4 P ¹ ,P 102.9 O ¹ ,P 94.7 N ¹ ,Cl 173.3	[17] EFODAE
	12 (14(14)		puplyiolp	P ¹ 2.21(1)	P ¹ ,N ¹ 82.7 N ¹ ,O ¹ 91.2	

Table

$\begin{array}{l} [Pt \kappa^3-Ph_2P^1(C_7H_6N^1=NCC^1.\\ C_5H_6)](CI)]\\ (at\ 150\ K) \end{array}$	tr Pī 2	7.431(2) 10.031(3) 14.797(5)	101.10(0) 95.70(0) 98.76(0)	$\begin{array}{c} {}^{PtP^1N^1N^2C}_{P^1C_3N^1NCN^2}_{0.038} \end{array}$		P ¹ ,N ² 173.0 P ¹ ,Cl 90.8 N ² ,Cl 94.2 N ¹ ,Cl 173.4	[15] XUYWEU
$\begin{array}{l} [Pt[\kappa^3 - Ph_2P^1(C_7H_5N^1)(C_7H_8N)\\ (C_7H_8N^2)](Cl)]PF_6 \end{array}$	P2 ₁ /c	18.910(3) 10.098(1) 19.429(3)	118.93(1)	${}^{{ m PtP}^1{ m N}^1{ m N}^2{ m Cl}}_{{ m P}^1{ m C}_3{ m N}^1{ m CN}^2}_{0.020}$	P ¹ 2.234(1) N ¹ 2.120(1) N ² 2.104(1) Cl 2.284(1)	P ¹ ,N ¹ 93.3 ^e N ¹ ,N ² 85.6 ^d P ¹ ,N ² 178.7 P ¹ ,Cl 91.8 N ² ,Cl 89.2 N ¹ ,Cl 174.0	[16] IFUQEF
B: $Pt(\kappa^3 - P^1N^1O^1)(Y)$							
$\begin{array}{l} [Pt(\kappa^{3}\text{-}Ph_{2}P^{1}(C_{8}H_{6}N^{1})(N.\\ C_{7}H_{5}O^{1})](\kappa^{1}\text{-}Ph_{2}P.\\ (C_{15}H_{12}N_{7}O)](.CH_{2}Cl_{2}\\ (at200\ K) \end{array}$	tr Pī 2	12.614(2) 13.671(2) 15.754(3)	100.26(0) 99.33(0) 110.68(0)	${}^{PtP^1N^1O^1P}_{\begin{array}{c}P^1C_2N^1NCO^1\\0.067\end{array}}$	P ¹ 2.233(2) N ¹ 1.985(2) O ¹ 2.050(2) LP 2.261(1)	P ¹ ,N ¹ 83.6 ^d N ¹ ,O ¹ 78.8 ^d P ¹ ,O ¹ 162.4 P ¹ ,P 102.9 O ¹ ,P 94.7 N ¹ ,Cl 173.3	[17] EFODAE
$\begin{array}{c} [Pt\{\kappa^3\text{-}Ph_2P^1(C_6H_4N^1).\\ (C_7H_4ClO^1)](P(p\text{-}tolyl_3)]ClO_4\\ (at\ 200\ K) \end{array}$	т Р2 ₁ /с 4	12.614(14) 20.280(20) 16.972(17)	98.96(1)	$\substack{PtP^1N^1O^1P\\P^1C_2N^1C_3O^1\\0.028}$	P ¹ 2.21(1) N ¹ 2.05(2) O ¹ 2.03(2) LP 2.269(1)	P ¹ ,N ¹ 82.7 N ¹ ,O ¹ 91.2 P ¹ ,O ¹ 172.1 P ¹ ,P 99.6 O ¹ ,P 86.5 N ¹ ,P 177.7	[18] KAVZOX
$[Pt(\kappa^{3}-Ph_{2}P^{1}(C_{6}H_{4}N^{1}).\\(C_{8}H_{7}OO^{1})]\\(Cl)]$	$P2_1/n$ 4	12.350(12) 12.138(14) 15.550(17)	97.70(1)	$\begin{array}{c} PtP^1N^1O^1Cl \\ P^1C_2N^1C_3O^1 \\ 0.007 \end{array}$	P ¹ 2.195(1) N ¹ 2.005(2) O ¹ 2.080(2) Cl 2.303(1)	P ¹ ,N ¹ 83.6 ^d N ¹ ,O ¹ 92.3 ^e P ¹ ,O ¹ 178.5 P ¹ ,Cl 93.5 O ¹ ,Cl 87.9 N ¹ ,Cl 178.9	[18] KAVZAJ
$\begin{split} & [Pt \{ \kappa^3 - Ph_2 P^1 (C_6 H_4 N^1). \\ & (C_8 H_7 OO^1)](I)](CH_2 Cl_2) \end{split}$	$P2_1/c$	10.446(11) 16.389(17) 16.507(0)	100.241(1)	$\begin{array}{c} PtP^{1}N^{1}O^{1}I\\P^{1}C_{2}N^{1}C_{3}O^{1}\\0.014\end{array}$	$\begin{array}{c} P^1 \; 2.207(1) \\ N^1 \; 2.011(2) \\ O^1 \; 2.045(2) \\ 1 \; 2.620(1) \end{array}$	P ¹ ,N ¹ 84.8 ^d N ¹ ,O ¹ 91.9 ^e P ¹ ,O ¹ 176.6 P ¹ ,I 92.6 O ¹ ,I 89.2 N ¹ ,I 178.2	[18] KAVZEN
$[Pt\{\kappa^3 - Ph_2P^1(C_8H_7N^1O^1)\}(Cl)]$	or Pna2 ₁ 4	18.88(2) 13.10(1) 9.66(1)		$\begin{array}{c} PtP^1N^1O^1Cl\\ P^1C_3N^1C_3O^1\\ 0.027 \end{array}$	P ¹ 2.206(1) N ¹ 1.88(1) O ¹ 2.14(1) Cl 2.386(4)	$\begin{array}{c} P^1, N^1 \; 94.8(4) \; ^e \\ N^1, O^1 \; 93.3(4) \; ^e \\ P^1, O^1 \; 175.5 \\ P^1, C1 \; 89.1(2) \\ O^1, C1 \; 84.0(2) \\ N^1, C1174.8 \end{array}$	[19] DERNIX
C: $Pt(\kappa^3 - P^1N^1C^1)(Y)$							
$[Pt[\kappa^{3}-Ph_{2}P^{1}(C_{7}H_{6}N^{1} = NC. \\ C^{1}C_{5}H_{6})](C1)] \\ (at 120 \text{ K})$	$P2_1/n$	8.632(4) 17.191(8) 15.216(7)	96.3(0)	PtP ¹ N ¹ C ¹ Cl P ¹ C ₂ N ¹ NCC ¹ 0.060	P ¹ 2.291(2) N ¹ 1.972(2) C ¹ 2.023(2) Cl 2.309(1)	$\begin{array}{c} P^1, N^1 \; 85.2 \; ^d \\ N^1, C^1 \; 78.7 \; ^d \\ P^1, C^1 \; 163.9 \\ P^1, C1 \; 99.9 \\ C^1, C1 \; 84.0 \\ N^1, C1174.6 \end{array}$	[20] YEHMOP
$\begin{array}{c} [Pt(\kappa^3-Ph_2P^1(C_7H_5N^1).\\ (C_7H_8C^1))(py)]BF_4\\ (at\ 100\ K) \end{array}$	m P2 ₁ 4	9.356(0) 19.892(1) 15.084(1)	90.76(0)	$\begin{array}{c} PtP^{1}N^{1}C^{1}N \\ P^{1}C_{3}N^{1}C_{2}C^{1} \\ 0.042 \end{array}$	P ¹ 2.292(1) N ¹ 2.000(2) C ¹ 2.035(2) pyN 2.026(1)	P ¹ ,N ¹ 92.1 ^e N ¹ ,C ¹ 82.3 ^d P ¹ ,C ¹ 174.3 P ¹ ,N 92.4 C ¹ ,N 93.6 N ¹ ,Cl170.7	[21] NIVCAX
D: $Pt(\kappa^3 - P^1N^1S^1)(Y)$							
$[Pt\{\kappa^3-Ph_2P^1(C_6H_4CHN^1NC. (S^1)NHMe](Cl)]$	$P2_1/c$	14.695(6) 16.683(7) 19.297(9)	102.83(6)	PtP ¹ N ¹ S ¹ C1 P ¹ C ₃ N ¹ NCS ¹ 0.022	P ¹ 2.239(5) N ¹ 2.03(2) S ¹ 2.298(5) Cl 2.304(5)	$\begin{array}{c} P^1, N^1 & \overline{95.8(4)} \ ^e \\ N^1 S^1 & 84.9(4) \ ^d \\ P^1 S^1 & 177.8(2) \\ P^1 C1 \ 89.5(2) \\ S^1, C1 \ 89.8(2) \\ N^1, C1174.4 \ (4) \end{array}$	[22] HAFMOQ
$[Pt\{\kappa^3-Ph_2P^1(C_7H_5N^1)(MeS^1).\\(Bu^1\cdot NH_2)](I)]$	tr Pī 2	10.529(1) 11.558(1) 14.550(1)	77.37(1) 84.45(1) 79.72(1)	${}^{PtP^1N^1S^1I}_{P^1C_3N^1C_3S^1}_{0.023}$	$\begin{array}{c} P^1 \; 2.240(2) \\ N^1 \; 2.056(6) \\ S^1 \; 2.363(2) \\ I \; 2.580(1) \end{array}$	$\begin{array}{c} P^{1}, N^{1} 89.1(1) \\ P^{1}, S^{1} 93.2(1) \\ P^{1}, S^{1} 176.2(2) \\ P^{1}, I 93.6(2) \\ S^{1}, I 84.2(2) \\ N^{1}, I 175.4(2) \end{array}$	[23] Robhop

Complex	Space gr. Cryst. cl. Z	a [Å] b [Å] c [Å]	α[°] β[°] γ[°]	Chromophore (Chelate Rings) T_4^{b}	Pt-L ^c [Å]	L-Pt-L ^c [°]	Ref. REFCODE
E: $Pt(\kappa^3 - P^1N^1Se^1)(Cl)$							
$\begin{array}{l} [Pt[\kappa^3\text{-}Ph_2P^1(C_7H_5N^1).\\ (C_3H_6\text{Se}^1)(Ph)](C1)]BF_4\\ (at\ 150K) \end{array}$	m P2 ₁ /c 4	9.869(0) 23.847(0) 11.740(0)	99.65(0)	$PtP^1N^1Se^1Cl$ $P^1C_3N^1C_3Se^1$ 0.012	$\begin{array}{c} P^1 \ 2.407(14) \\ N^1 \ 2.028(4) \\ Se^1 \ 2.489(1) \\ Cl \ 2.308(1) \end{array}$	$\begin{array}{c} P^1, N^1 \; 87.5(1) \;^e \\ N^1 \; Se^1 \; 95.7(1) \;^e \\ P^1 \; Se^1 \; 176.7(1) \\ P^1, Cl \; 93.0(1) \\ Se^1, Cl \; 83.7(1) \\ N^1, Cl \; 178.8(1) \end{array}$	[24] MULZIC

Table 1. Cont.

Footnotes: ^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d. and the second is the maximum deviation from the mean. ^b Parameter T_4 , degree of distortion. ^c The chemical identity of the coordinated atom ligand is specific in these columns. ^d Five-membered metallocyclic ring. ^e Six-membered metallocyclic ring.

In following six complexes: triclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₂H₂O)N²(C₆H₄OH)}(CH₃)]. CHCl₃ (at 150 K) [11], monoclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₂H₂O)N²(C₆H₆OH)}(CH₃)].1.5toluene (at 150 K) [11] [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₃H₆)N²(C₇H₅O₂)}(CH₃)].2 toluene (at 150 K) [11], monoclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₆H₄)N²(C₁₀H₉NO₃)](CH₃)].Et₂O (at 150 K) [12], monoclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₅H₇O)N²(C₁₀H₁₀N₂)](CH₃)].H₂O (at 93 K) [13], and monoclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₂H₂O)N²(C₆H₄OH)}(CH₃)].CHCl₃ (at 150 K) [14] each κ^3 -P¹N¹N² ligand creates six- and five-metallocyclic rings with the centre common ligating N¹ atom of the P¹C₃N¹C₂N² type. In each complex the methyl group completed a distorted square-planar geometry about each Pt(II) atom. The mean values for the respective chelate rings are: 93.8(±4.0)° (P¹-Pt-N¹) and 80.3(±1.2)° (N¹-Pt-N²). The remaining L-Pt-L bind angles open in the sequence (mean values): 90.9(1.9)° (P¹-Pt-C) < 94.4(2.2)° (N²-Pt-C) < 173.4(1.3)° (N¹-Pt-C) < 173.7(4.7)° (P¹-Pt-N²). The Pt-L bond distance elongates in the order (mean values): 2.060(±23)Å (Pt-C, trans to N¹) < 2.066(±21)Å (Pt-N¹, trans to C) < 2.079(±15)Å (Pt-N², trans to P¹) < 2.186(±7)Å (Pt-P¹, trans to N²).

The structure of the triclinic $[Pt{\kappa^3-Ph_2P^1(C_7H_5N^1)(NC_5H_4N^2)}(Cl)]$ (at 150 K) is shown in Figure 1, as an example [15]. As can be seen, the $\kappa^3-P^1N^1N^2$ ligand forms sixand five-membered metallocyclic rings of the $P^1C_3N^1NCN^2$ type with the centre common ligating N¹ atom. The chlorido ligand completed a distorted square-planar geometry about the Pt(II)atom. The values of the respective rings are 95.8° (P¹-Pt-N¹) and 79.3° (N¹-Pt-N²). The remaining bind angles open in the sequence: 90.8° (P¹-Pt-Cl) < 94.2° (N²-Pt-Cl) < 173.0° (P¹-Pt-N²) < 173.4° (N¹-Pt-Cl). The Pt-L bond distance elongates in the order: 2.053 Å (Pt-N¹, trans to Cl) < 2.086 Å (Pt-N², trans to P¹) < 2.200 Å (Pt-P¹) < 2.297 Å (Pt-Cl).

In the monoclinic $[Pt{\kappa^3-Ph_2P^1(C_7H_6N^1)(C_7H_8N)(C_7H_8N^2)}(Cl)].PF_6$ [16] the $\kappa^3-P^1N^1N^2$ ligand creates two six-membered metallocyclic rings with the centre common ligating N¹ atom of the $P^1C_3N^1C_3N^2$ type. The values of the chelate rings are 93.3° (P1-Pt-N1) and 85.6°(N¹-Pt-N²). The remaining bind angles open in the order: 90.9° (N²-Pt-Cl) < 91.8° (P¹-Pt-Cl) < 174.0° (N¹-Pt-Cl) < 178.7° (P¹-Pt-N²). The Pt-L bond distance elongates in the order: 2.104 Å (Pt-N², trans to P¹) < 2.120 Å (Pt-N¹, trans to Cl) < 2.234 Å (Pt-P¹) < 2.284 Å (Pt-Cl).

2.2. $Pt(\kappa^3 - P^1N^1O^1)(Y)$ Derivatives

Structural data for five Pt(κ^3 –P¹N¹O¹)(Y) derivatives are gathered in Table 1 (B: Pt(κ^3 –P¹N¹O¹)(Y)). In the triclinic [Pt{ κ^3 –Ph₂P¹(C₈H₆N¹)(NC₇H₅O¹)}{ κ^1 –Ph₂P(C₁₅H₁₃N₂O)}].CH₂Cl₂ (at 200 K) [17] the κ^3 –P¹N¹O¹ ligand with monodentate PL donor ligand builds up a distorted square-planar geometry about the Pt(II) atom (PtP¹N¹O¹P). The κ^3 –P¹N¹O¹ ligand forms two five-membered metallocyclic rings with the centre common ligating N¹ atom of the P¹C₂N¹NCO¹ type, with the values of the chelate rings of 83.6° (P¹-Pt-N¹) and 78.8° (N¹-Pt-O¹). The remaining L-Pt-L bind angles open in the sequence: 94.7° (O¹–Pt–P) < 102.9° (P¹–Pt–P) < 162.4° (P¹–Pt–O¹) < 173.3° (N¹–Pt–P). The Pt-L bond distance elongates

in the order: 1.985 Å (Pt–N¹, trans to P) < 2.050 Å (Pt–O¹, trans to P¹) < 2.233 Å (Pt–P¹) < 2.261 Å (Pt–P).



Figure 1. Structure of $[Pt{\kappa^3-Ph_2P^1(C_7H_6N^1)(NC_5H_5N^2)}(Cl)]$ [15].

In the monoclinic $[Pt{\kappa^3-Ph_2P^1(C_6H_4N^1)(C_7H_4ClO^1)}{P(p-tolyl)_3}].ClO_4$ (at 200 K) [18] a distorted square-planar geometry about the Pt(II) atom is built up by the $\kappa^3-P^1N^1O^1$ ligand with P(p-tolyl)_3. The $\kappa^3-P^1N^1O^1$ ligand forms five- and six-membered metallocyclic rings with the common N¹ atom of the $P^1C_2N^1C_3O^1$ type with the values of the chelate rings of 82.7° (P¹-Pt-N¹) and 91.2° (N¹-Pt-O¹). The remaining L-Pt-L bind angles open in the order: 86.5° (O¹-Pt-P) < 99.6° (P¹-Pt-P) < 172.1° (P¹-Pt-O¹) < 177.7° (N¹-Pt-P). The Pt-L bond distance elongates in the order: 2.03 Å (Pt-O¹ trans to P¹) < 2.05 Å (Pt-N¹ trans to P) < 2.21(1) Å (Pt-P¹) < 2.269 Å (Pt-P).

Two monoclinics $[Pt\{\kappa^3-Ph_2P^1(C_6H_4N^1)(C_8H_7OO^1)\}(Z)]$ (Z = Cl or I) are isostructural [18]. The $\kappa^3-P^1N^1O^1$ with Z builds up distorted square-planar geometry about the Pt(II) atoms. The values of $P^1C_2N^1C_3O^1$ metallocyclic rings are 83.6° (P^1 -Pt- N^1) and 92.3° (N^1 -Pt- O^1) when Z = Cl; for Z = I, the values are 84.8° and 91.9°, respectively. The remaining L-Pt-L bind angles open in the order: 87.9° (O^1 -Pt-Cl) < 93.5° (P^1 -Pt-Cl) < 178.5° (P^1 -Pt- O^1) < 178.9° (N^1 -Pt-Cl); vs. 89.2° (O^1 -Pt-I) < 92.6° (P^1 -Pt-I) < 176.6° (P^1 -Pt- O^1) < 178.2° (N^1 -Pt-I). As can be seen, the L-Pt-L angles for Cl^- complex are somewhat larger than for I^- complex, except O^1 -Pt-X. The Pt-L bond distance elongates in the order: 2.005 Å ($Pt-N^1$, trans to Cl) < 2.080 Å ($Pt-O^1$, trans to P^1) < 2.207 Å ($Pt-P^1$) < 2.620 Å (Pt-I).

In orthorhombic [Pt{ κ^3 -Ph₂P¹(C₈H₇N¹O¹)}(Cl)] [19], the κ^3 -P¹N¹O¹ ligand form two six-membered metallocyclic rings of the P¹C₃N¹C₃O¹ type with the central common ligating N¹ atom. The clorido ligands completed a distorted square-planar geometry about the Pt(II) atom. The values of the chelate rings are 94.8° (P¹-Pt-N¹) and 93.3° (N¹-Pt-O¹). The remaining L-Pt-L bind angles open in the order: 84.0° (O¹-Pt-Cl) < 89.1° (P¹-Pt-Cl) < 174.8° (N¹-Pt-Cl) < 175.5° (P¹-Pt-O¹). The Pt-L bond distance elongates in the order: 1.88 Å (Pt-N¹, trans to Cl) < 2.14 Å (Pt-O¹, trans to P¹) < 2.206 Å (Pt-P¹) < 2.386 Å (Pt-Cl).

2.3. $Pt(\kappa^3 - P^1N^1C^1)(Y)$ Derivatives

There are two monoclinic complexes $[Pt{\kappa^3-Ph_2P^1(C_7H_6N^1 = NCC^1C_5H_6)}(Cl)]$ (Figure 2) (at 120 K) [20] and $[Pt{\kappa^3-Ph_2P^1(C_7H_5N^1)(C_7H_8C^1)}(py)]$.BF₄ (at 100 K) [21] (Table 1 (C: Pt($\kappa^3-P^1N^1C^1$)(Y))). In the former complex, the $\kappa^3-P^1N^1C^1$ ligand forms two five-membered metallocyclic rings of the $P^1C_2N^1NCC^1$ type, with the values of the chelate rings of 85.2° (P¹-Pt-N¹) and 78.7° (N¹-Pt-C¹), respectively. The clorido ligands completed a distorted square-planar geometry about the Pt(II) atom. The remaining L-Pt-L bind angles open in the order: 84.0° (C¹-Pt-Cl) < 99.9° (P¹-Pt-Cl) < 163.9° (P¹-Pt-C¹) < 174.6° (N¹-Pt-Cl). The Pt-L bond distance elongates in the order: 1.972 Å (Pt-N¹, trans to Cl) < 2.023 Å (Pt-C¹, trans to P¹) < 2.291 Å (Pt-P¹) < 2.309 Å (Pt-Cl).



Figure 2. Structure of $[Pt{\kappa^3-Ph_2P^1(C_7H_6N^1 = NCC^1C_5H_6)}(Cl)]$ [20].

In the complex cation, the N-donor atom of pyridine completed the inner coordination sphere about the Pt(II) atom (PtP¹N¹C¹N). The κ^3 -ligand creates six- and five-membered metallocycles of the P¹C₃N¹C₂C¹ type. The values of the respective chelate rings are 92.1° (P¹-Pt-N¹) and 82.3° (N¹-Pt-C¹). The remaining L-Pt-L bind angles open in the order: 92.4° (P¹-Pt-N) < 93.6° (C¹-Pt-N) < 170.7° (N¹-Pt-Cl) < 174.3° (P¹-Pt-C¹). The Pt-L bond distance elongates in the order: 2.000 Å (Pt-N¹ trans to N) < 2.026 Å (Pt-N¹) < 2.035 Å (Pt-C¹, trans to P¹) < 2.292 Å (Pt-P¹).

2.4. $Pt(\kappa^3 - P^1N^1S^1)(Y)$ Derivatives

There are two such derivatives, monoclinic $[Pt\{\kappa^3-Ph_2P^1(C_6H_4CHN^1NC(S^1) NHMe\}$ (Cl)] [22] and triclinic $[Pt\{\kappa^3-Ph_2P^1(C_7H_5N^1)(MeS^1)(Bu^tNH_2)\}(I)]$ [23] (Table 1 (D: $Pt(\kappa^3-P^1N^1S^1)(Y)$)). In the monoclinic complex, the $\kappa^3-P^1N^1S^1$ ligand with chlorido builds up distorted square-planar geometry about the Pt(II) atom. The $\kappa^3-P^1N^1S^1$ ligand in the chlorido complex creates six- and five-membered metallocyclic rings with the centre common ligating N^1 atom of the $P^1C_3N^1NCS^1$ type. The values of the chelate rings are 95.8° (P^1-Pt-N^1) and 84.9° (N^1-Pt-S^1). The remaining L-Pt-L bind angles open in the order: 89.5° ($P^1-Pt-Cl$) < 89.8° ($S^1-Pt-Cl$) < 174.4° ($N^1-Pt-Cl$) < 177.8° (P^1-Pt-S^1). The Pt-L bond distance elongates in the order: 2.03 Å ($Pt-N^1$, trans to Cl) < 2.239 Å ($Pt-P^1$, trans to S^1) < 2.298 Å ($Pt-S^1$) < 2.304 Å (Pt-Cl).

In the triclinic complex, the κ^3 – $P^1N^1S^1$ ligand creates two six-membered metallocyclic rings of the $P^1C_3N^1C_3S^1$ type with the values of the chelate rings of 89.1° (P^1 -Pt- N^1) and

93.2° (N¹-Pt-S¹). The remaining L-Pt-L bind angles open in the order: 84.2° (S¹–Pt–I) < 93.6° (P¹–Pt–I) < 175.4° (N¹–Pt–I) < 176.2° (P¹–Pt–S¹). The Pt-L bond distance elongates in the order: 2.056 Å (Pt–N¹, trans to I) < 2.240 Å (Pt–P¹, trans to S¹) < 2.363 Å (Pt–S¹) < 2.580 Å (Pt–I).

2.5. $Pt(\kappa^3 - P^1N^1Se^1)(Y)$ Derivatives

Monoclinic [Pt{ κ^3 -Ph₂P¹(C₇H₅N¹)(C₃H₆Se¹)(Ph)}(Cl)].BF₄ (at 150 K) [24] is the only example of κ^3 -P¹N¹Se¹ type. The Cl⁻ anion completed a distorted square-planar geometry about the Pt(II) atom. The κ^3 -P¹N¹Se¹ ligand creates two six-membered metallocyclic rings with the centre common ligating N¹ atom of the P¹C₃N¹C₃Se¹ type. The values of the chelate rings are 87.5° (P¹-Pt-N¹) and 95.7° (N¹-Pt-Se¹). The remaining L-Pt-L bind angles open in the order: 83.7° (Se¹-Pt-Cl) < 93.0° (P¹-Pt-Cl) < 176.7° (P¹-Pt-Se¹) < 178.8° (N¹-Pt-Cl). The Pt-L bond distance elongates in the order: 2.028 Å (Pt-N¹, trans to Cl) < 2.308 Å (Pt-Cl) < 2.407 Å (Pt-P¹, trans to Se¹) < 2.489 Å (Pt-Se¹).

2.6. $Pt(\kappa^3 - N^1P^1N^2)(Cl)$ and $Pt(\kappa^3 - S^1P^1S^2)(Cl)$ Derivatives

Their structural data are gathered in Table 2. In orthorhombic [Pt{ $\kappa^3-N^1(C_6H_6)N(C_6H_{10})NP^1(Pr^i)(C_6H_6)N^2$ }(Cl)]Cl.H₂O (at 150 K) [25] heterotridentate $\kappa^3-N^1P^1N^2$ ligand with Cl⁻ anion builds up a distorted square-planar geometry about the Pt(II) atom. The $\kappa^3-N^1P^1N^2$ ligand forms two six-membered metallocyclic rings with the centre common ligating P¹ atom of the $N^1C_2NP^1NC_2N^2$ type. The values of the chelate rings are: 91.1° (N¹-Pt-P¹) and 91.0° (P¹-Pt-N²). The remaining L-Pt-L bind angles open in the order: 90.4° (N¹-Pt-Cl) < 91.0° (N²-Pt-Cl) < 173.0° (P¹-Pt-Cl) < 175.4° (N¹-Pt-N²). The Pt-L bond distance elongates in the order: 2.035 Å (Pt-N¹, trans to N²) < 2.039 Å (Pt-N²) < 2.187 Å (Pt-P¹. trans to Cl) < 2.375 Å (Pt-Cl).

Table 2. Data for $Pt(\kappa^3 - X^1P^1X^2)(Cl)$, $Pt(\kappa^3 - P^1S^1Cl^1)(Cl)$ and $Pt(\kappa^3 - P^1Si^1N^1)(OL)$ derivatives monodentate atoms/ligands)^a.

Complex	Space gr. Cryst. cl. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore (Chelate Rings) T_4^{b}	Pt-L ^c [Å]	L-Pt-L ^c [°]	Ref. REFCODE
$\begin{array}{c} [Pt[\kappa^3-N^1(C_6H_6)N(C_6H_{10})N\\ P^1(Pr^i) \ (C_6H_6)N^2[(Cl)].H_2O\\ (at\ 150\ K) \end{array}$	$\operatorname{P2_{12_{1}2_{1}}}_{6}^{\operatorname{or}}$	14.373(0) 9.906(0) 17.590(0)		$\begin{array}{c} PtN^{1}P^{1}N^{2}Cl\\ N^{1}C_{2}NP^{1}NC_{2}N^{2}\\ 0.032 \end{array}$	N ¹ 2.035 P ¹ 2.187 N ² 2.039 Cl 2.375	N ¹ ,P ¹ 91.1 ^e P ¹ ,N ² 91.0 ^e N ¹ ,N ² 175.4 N ¹ ,Cl 90.4 N ² ,Cl 91.0 P ¹ ,Cl 173.0	[25] IRAWOO
$\begin{array}{c} [\mathrm{Pt}\{\kappa^3\mathrm{-}\mathrm{Pr}^i\mathrm{S}^1(\mathrm{C}_6\mathrm{H}_4)\mathrm{P}^1.\\ (\mathrm{C}_6\mathrm{H}_4\mathrm{S}\mathrm{Pr}^i)\ (\mathrm{C}_6\mathrm{H}_4)\mathrm{S}^2](\mathrm{Cl})]\\ (\mathrm{at}\ 123\ \mathrm{K}) \end{array}$	$P2_1/n$	8.790(0) 18.706(1) 15.508(1)	95.89(0)	$\begin{array}{c} PtS^{1}P^{1}S^{2}Cl\\S^{1}C_{2}P^{1}C_{2}S^{2}\\0.055\end{array}$	$\begin{array}{c} S^1 \ 2.289 \\ P^1 \ 2.189 \\ S^2 \ 2.292 \\ Cl \ 2.374 \end{array}$	S ¹ ,p ¹ 88.2 d P ¹ ,S ² 87.7 d S ¹ ,S ² 162.1 S ¹ ,Cl 93.0 S ² ,Cl 90.8 P ¹ ,Cl 178.3	[26] EZORAO
$\begin{array}{c} [Pt[\kappa^3\text{-}Bu^tS^1(C_6H_4)P^1.\\ (C_6H_4SBu^t)(C_6H_4)S^2](C1)].0.5CHCl_3\\ (at 123 \ K) \end{array}$	$p_{2_1/n}^{m}$	10.250(1) 18.715(2) 15.320(1)	96.65(0)	$\begin{array}{c} PtS^{1}P^{1}S^{2}Cl\\ S^{1}C_{2}P^{1}C_{2}S^{2}\\ 0.063 \end{array}$	$\begin{array}{c} S^1 \ 2.287 \\ P^1 \ 2.198 \\ S^2 \ 2.297 \\ Cl \ 2.360 \end{array}$	S ¹ , p ¹ 88.7 ^d p ¹ , S ² 88.8 ^d S ¹ , S ² 158.7 N ¹ , Cl 92.8 N ² , Cl 90.8 P ¹ , Cl 178.6	[26] EZOQIV
$\begin{array}{c} [Pt(\kappa^{3}\text{-}Ph_{2}P^{1}(C_{23}H_{28}S^{1}).\\ (B)(Ph_{2})Cl^{1})](C1)].2CH_{2}Cl_{2}\\ (at\ 123\ K) \end{array}$	or Pna2 ₁ 4	21.373(0) 8.959(0) 25.330(3)		PtP ¹ S ¹ Cl ¹ Cl P ¹ C ₂ S ¹ C ₂ BCl ¹ 0.033	$\begin{array}{c} P^1 \ 2.212 \\ S^1 \ 2.243 \\ Cl^1 \ 2.391 \\ Cl^2 \ 2.321 \end{array}$	P ¹ ,S ¹ 87.9 ^d S ¹ ,Cl ¹ 87.1 ^e P ¹ ,Cl ¹ 174.7 P ¹ ,Cl 93.4 Cl ¹ ,Cl 91.7 S ¹ ,Cl 173.3	[27] DASMER
$\begin{array}{c} [Pt[\kappa^3\text{-}cyh_2P^1(C_6H_4)Si^1.\\ (CH_3)(C_7H_6)N^1(CH_3)_2)].\\ (OSO_2CF_3)]\\ (at 123\ K) \end{array}$	P2 ₁ /c	19.851(1) 20.837(3) 15.443(2)	99.52(0)	$\begin{array}{c} PtP^{1}Si^{1}N^{1}O\\ P^{1}C_{2}Si^{1}C_{3}N^{1}\\ 0.033 \end{array}$	P ¹ 2.228 Si ¹ 2.260 N ¹ 2.177 LO 2.353	P ¹ ,Si ¹ 85.8 ^d Si ¹ ,N ¹ 82.7 ^e P ¹ ,N ¹ 169.2 P ¹ ,O 95.0 N ¹ ,O 86.4 Si ¹ ,O 179.0	[28] WUXFAI

Footnotes: ^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d. and the second is the maximum deviation from the mean. ^b Parameter T_4 , degree of distortion. ^c The chemical identity of the coordinated atom ligand is specific to these columns. ^d Six- membered metallocyclic ring. ^e Five-membered metallocyclic ring.

Two monoclinic complexes $[Pt\{\kappa^3-Pr^iS^1(C_6H_4)P^1(C_6H_4SPr^i)(C_6H_4)S^2\}(Cl)]$ (Figure 3) (at 123 K) [26] and $[Pt\{\kappa^3-Bu^tS^1(C_6H_4)P^1(C_6H_4SBu^t)(C_6H_4)S^2\}(Cl)]$.0.5CHCl₃ (at 123 K) [26] have a similar structure. In each, the $\kappa^3-S^1P^1S^2$ ligand forms two five-membered metallocycles with the centre common ligating P¹ atom of the $S^1C_2P^1C_2S^2$ type. In the former complex, the values of the chelate rings are 88.2° (S¹-Pt-P¹) and 87.7° (P¹-Pt-S²). The remaining L-Pt-L angles open in the order: 90.8° (S²-Pt-Cl) < 93.0° (S¹-Pt-Cl) < 162.1° (S¹-Pt-S²) < 178.3° (P¹-Pt-Cl). In the latter complex, the L-Pt-L angles open in the order: 88.7° (S¹-Pt-P¹) < 88.8° (P¹-Pt-S²) < 90.8° (S²-Pt-Cl) < 158.7° (S¹-Pt-S²) < 178.6° (P¹-Pt-Cl).



Figure 3. Structure of $[Pt\{\kappa^3 - Pr^iS^1(C_6H_4)P^1(C_6H_4SPr^i)(C_6H_4)S^2\}(Cl)]$ [26].

The Pt-L bond distance elongates in the order (mean values): $2.194(\pm 4)$ Å (Pt–P¹, trans to Cl) < 2.288 Å (Pt-S¹ trans to S²) < $2.294 (\pm 3)$ Å (Pt–S²) < $2.367 (\pm 7)$ Å (Pt–Cl).

2.7. $Pt(\kappa^3 - P^1S^1Cl^1)(Cl)$ and $Pt(\kappa^3 - P^1Si^1N^1)(OL)$ Derivatives

Their structural data are given in Table 2. In the orthorhombic [Pt{ κ^3 -Ph₂P¹(C₂₃H₂₈S¹) (B)(Ph₂)Cl¹}(Cl)]·2CH₂Cl₂ (Figure 4) (at 123 K) [27] heterotridentate κ^3 -P¹S¹Cl¹ ligand with the Cl⁻ anion builds up a distorted square-planar geometry about the Pt(II) atom. The κ^3 -P¹S¹Cl¹ forms five- and six-metallocyclic rings of the P¹C₂S¹C₂BCl¹ type. The values of the respective chelate rings are 87.9° (P¹-Pt-S¹) and 87.1° (S¹-Pt-Cl¹). The remaining L-Pt-L bind angles open in the order: 91.7° (Cl¹-Pt-Cl) < 93.4° (P¹-Pt-Cl) < 173.3° (S¹-Pt-Cl) < 174.7° (P¹-Pt-Cl¹). The Pt-L bond distance elongates in the order: 2.212 Å (Pt-P¹, trans to Cl¹) < 2.243 Å (Pt-S¹, trans to Cl) < 2.321 Å (Pt-Cl) < 2.391 Å (Pt-Cl¹).

Structure of the monoclinic [Pt{ κ^3 -cyh₂P¹(C₆H₄)Si¹(CH₃)(C₇H₆)N¹(CH₃)₂}(OSO₂CF₃)] [28] is shown in Figure 5. The κ^3 -P¹Si¹N¹ ligand with OL builds up a distorted square-planar geometry about the Pt(II) atom. The chelate ligand forms five- and six-membered metallocyclic rings with the central common ligating Si¹ atom of the P¹C₂Si¹C₃N¹ type. The values of the respective angles are 85.8° (P¹-Pt-Si¹) and 82.7° (Si¹-Pt-N¹). The remaining L-Pt-L bind angles open in the order: 86.4° (N¹-Pt-O) < 95.0° (P¹-Pt-O) < 169.2° (P¹-Pt-N¹) <



179.0° (Si¹–Pt–O). The Pt-L bond distance elongates in the order: 2.177 Å (Pt–N¹, trans to P¹) < 2.228 Å (Pt–P¹) < 2.260 Å (Pt–Si¹, trans to O) < 2.353 Å (Pt–O).

Figure 4. Structure of $Pt\{\kappa^3 - Ph_2P^1(C_{23}H_{28}S^1)(B)(Ph_2)Cl^1\}(Cl)]$ [27].



 $\label{eq:Figure 5. Structure of [Pt{κ^3-cyh_2P^1(C_6H_4)Si$^1(CH_3)(C_7H_6)N$^1(CH_3)_2}(OSO_2CF_3)] \end{tabular} \end{tabular} \end{tabular} \end{tabular}$

As can be seen (Tables 1 and 2), organomonophosphines as heterotridentate ligands used (except for the P atom) a wide variety of heteroatoms for coordination to Pt(II) atoms. There are twenty four Pt(II) complexes which crystalized in three crystal classes: monoclinic (16 examples), triclinic (5 examples) and orthorhombic (3 examples). Each heterotridentate ligand forms two metallocyclic rings. The metallocycles based on the heteroatom involved in these metallocycles can divided into four subgroups:

- I. 5 + 5—membered: P1C2P1C2N2 (1 example), P1C2N1NCO1 (1 example), P¹C₂N¹NCC¹ (1 example) and S¹C₂N¹C₂S² (2 examples)
- II. 6+5—membered: P1C3N1C2N2 (6 examples), P1C3N1NCN2, (1 example), P1C3N1C2C1, (1 example) and P1C3N1NCS1 (1 example)
- III. 5 + 6—membered: P1C2N1C3O1 (3 examples), P1C2S1C2BCl1, (1 example) and P1C2Si1C3N1 (1 example)
- IV. 6 + 6—membered: $P^1C_3N^1C_3N^2$, $P^1C_3N^1C_3O^1$, $P^1C_3N^1C_3S^1$, $P^1C_3N^1C_3Se^1$ and $N^1C_2NP^1NC_2N^2$ (each 1 example)

In the Pt(κ^3 –P¹N¹X)(Y), (X = N², O¹, C¹, S¹, or Se¹) complexes (Table 1) the total mean values of Pt-L bind distance elongate in the sequences:

Pt-P¹ (trans to X): 2.20 Å (N²) < 2.22 Å (O¹) < 2.23 Å (C¹) < 2.24 Å (S¹) < 2.40 Å (Se¹); Pt-X¹ (trans to P¹): 2.03 Å (C¹) < 2.065 Å (O¹) < 2.085 Å (N²) < 2.330 Å (S¹) < 2.489 Å (Se¹); Pt-N¹ (trans to Y): 1.985 Å (P²) < 2.00 Å (N³) < 2.02 Å (Cl) < 2.03 Å (I) < 2.065 Å (C²); Pt-Y¹ (trans to N¹): 2.005 Å (N³) < 2.068 Å (C²) < 2.260 Å (P²) < 2.304 Å (Cl) < 2.600 Å (I). These correspond quite were with the *trans* influence of the X¹ /ligand.

3. Conclusions

This review covers 24 monomeric four-coordinated Pt(II) complexes. The inner coordination sphere about the Pt(II) atoms are built up heterotridentate organomonophosphines with the monodentate atom/ligand. The κ^3 —ligands create a variety of metallocyclic rings.

There are at least two contributing factors to the size of the L-Pt-L chelate bond angles, both ligand based. One is steric constraints imposed by the ligand, and the other is the need to accommodate the imposed ring size. The effect of both steric and electronic can be seen from the values of the chelate angles (mean values):

5 + 5—membered

 $P^{1}C_{2}N^{1}/N^{1}NCO^{1}\,83.6/78.8^{\circ}; P^{1}C_{2}N^{1}/N^{1}NCC^{1}\,85.2/78.7^{\circ}; S^{1}C_{2}P^{1}/P^{1}C_{2}S^{2}\,88.5/88.2^{\circ}; P^{1}C_{2}N^{1}/N^{1}C_{2}N^{2}\,85.5/83.4^{\circ}$

6 + 5—membered

 $P^{1}C_{3}N^{1}/N^{1}C_{2}C^{1} 92.1/82.3^{\circ}; P^{1}C_{3}N^{1}/N^{1}C_{2}N^{2} 93.8/80.2^{\circ}; P^{1}C_{3}N^{1}/N^{1}NCN^{2} 94.5/82.5^{\circ}; P^{1}C_{3}N^{1}/N^{1}NCS^{1} 95.8/84.9^{\circ};$

5 + 6 membered

 $P^{1}C_{2}Si^{1}/Si^{1}C_{3}N^{1} 85.6/82.7^{\circ}; P^{1}C_{2}S^{1}/S^{1}C_{2}BCl^{1} 87.9/87.1^{\circ}; P^{1}C_{2}N^{1}/N^{1}C_{3}O^{1} 83.7/91.8^{\circ} 6 + 6 \text{ membered}$

 $N^{1}C_{2}NP^{1}/P^{1}NC_{2}N^{2} \ 91.1/91.0^{\circ}; P^{1}C_{3}N^{1}/N^{1}C_{3}O^{1} \ 94.8/93.3^{\circ}; P^{1}C_{3}N^{1}/N^{1}C_{3}S^{1} \ 89.1/93.2^{\circ}; P^{1}C_{3}N^{1}/N^{1}C_{3}Se^{1} \ 82.5/95.2^{\circ}$

It is well known that in four coordinates, Pt(II) prefer a square-planar geometry. The utility of a simple metric to assess molecular shape and degree of distortion as well is best exemplified by the T_4 parameter for a square-planar geometry by the equation introduced by the [29].

 $T_4 = 360 - (\alpha + \beta)/360$ for square-planar, and

 $T_4 = 360 - (\alpha + \beta)/141$ for tetrahedral

The values for T_4 range from 0.00 for perfect square-planar geometry to 1.00 for a perfect tetrahedral, since 360 - 2 (109.5)/141.

Summary of the total mean values of *trans-* α - L-Pt-L (L are terminal ligating atoms of the respective chelate) and *trans-* β - L'-Pt-Y (L' central ligating atom of the rings) bond angles and of T₄ are given in Table 3.

As can be seen (Table 3) where β -angles are almost constant, the α -angles are mostly growing with the membered of the respective rings. The distortion of the square- planar geometry about the Pt(II) atoms is diminishing.

Table 3. Summary of metallocyclic rings, *trans*-L-Pt-L angles and parameter T₄.

Metallocyclic Rings	α- L-Pt-L [°]	β - Ľ′-Pt- Υ [°]	T4
5 + 5—membered	163.0	176.2	0.058
6 + 5—membered	172.9	173.6	0.037
5 + 6—membered	174.2	177.5	0.023
6 + 6—membered	176.5	175.6	0.022

In general, distortion of the square-planar geometry about the Pt(II) atoms is diminishing in the order of the respective complexes (total mean values): 0.059 (PtS¹P¹S²)(Y) > 0.051 (PtP¹N¹C¹)(Y) > 0.033 (PtP¹Si¹N¹)(Y) ~ 0.033 (PtP¹S¹Cl¹)(Y) > 0.032 (PtN¹P¹N²)(Y) > 0.028 (PtP¹N¹O¹)(Y) > 0.023 (PtP¹N¹S¹)(Y) > 0.012 (PtP¹N¹Se¹)(Y)

Noticeably, in some complexes there is a relationship between the inner coordination sphere about the Pt(II) atom and the degree of distortion. When the volume of the inner coordination sphere is growing, the distortion is lowering and vice versa, as can be seen from the parameters of the sums of the four Pt-L bond distances and parameters of T_4 . The (Pt-L(x4) vs. T_4) are:

 $Pt(\kappa^3 - P^1N^1N^2)(Y)$: 8.394 Å vs. 0.036(Y = CL); 8.647 Å vs. 0.034 (Y = Cl)

Pt(κ^3 –P¹N¹O²)(Y): 8.556 Å vs. 0.048(Y = PL); 8.594 Å vs. 0.011 (Y = Cl); 8.883 Å vs. 0.014 (Y = I)

 $\begin{array}{l} Pt(\kappa^{3}-P^{1}N^{1}S^{1})(Y){:}\;8.891\;\text{\AA vs.}\;0.023\;(Y=Cl); 9.231\;\text{\AA vs.}\;0.022\;(Y=I)\\ Pt(\kappa^{3}-P^{1}N^{1}Se^{1})(Cl){:}\;9.226\;\text{\AA vs.}\;0.012 \end{array}$

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Abbreviations

$Bu_{2}^{t}P^{1}(CH_{2})(C_{5}H_{3}N^{1})(CH_{2})N^{2}Et_{2}$	(2-(di-t-butylphosphinomethyl)-6-diethyl- aminomethyl)pyridine)
$Bu^{t}S^{1}(C_{6}H_{4})P^{1}(C_{6}H_{4}SBu^{t})(C_{6}H_{4})S^{2})$	(2-((2-(t-butylsulfanyl)phenyl)(2-t-butyl-sulfanyl) phenyl)phosphino)benzenethiazato
$cyh_2P^1(C_6H_4)Si^1(CH_3)(C_7H_6N^1(Me_2))$	((2-(dicyclohexylphosphanyl)(2-(dimethyl-amino) methyl)phenyl)methylsilyl)
m	monoclinic
$N^{1}(C_{6}H_{6})N(C_{6}H_{10})NP^{1}(Pr^{i})(C_{6}H_{6})N^{2}$	(2-isopropyl-1,3-bis(2-pyridylmethyl)-octahydro- 1H-1,3,2-benzodiazophosphore
or	orthorhombic
Ph ₂ P ¹ ((C ₆ H ₄ CHN ¹ NC(S ¹).NHMe)	(2-(diphenylphosphino)thiosemicarbazide
$Ph_2P^1(C_{23}H_{28}S^1)(B(Ph_2)Cl^1)$	((2,7-di-t-butyl-5-((chloro)(diphenyl)-2 ⁵ -boranyl)-
	9,9-dimethyl-9H-thioxantin-4-yl)(diphonylphosphine)

$Ph_2P^1(C_6H_4N^1)(C_7H_4ClO^1)(C_7H_8N^2)$	(4-chloro-2-(((2-(diphenylphosphino)phenylimino)
	methylphenylate
$Ph_2P^1(C_6H_4N^1)(C_8H_7NOO^1)$	(2-(((2-(diphenylphosphino)phenylimino)methyl-
	4-methoxyphenylato)
$Ph_2P^1(C_7H_5N^1)(C_2H_2O)N^2(C_6H_4OH)$	(N-(2-(diphenylphosphinobenzylidene)-N-
	(2-hydroxyphenyl)glycinamidato)
$Ph_2P^1(C_7H_5N^1)(C_2H_2O)N^2(C_6H_4OH)$	(N ² -(2-(diphenylphosphino)benzylidene)-N-
	(3-hydroxyphenyl)glycinamidato
$Ph_2P^1(C_7H_5N^1)(C_2H_2O)N^2(C_7H_6OH)$	(N-(2-(diphenylphosphino)benzylidene)-N-
	(2-hydroxymethylphenyl)glycine-amidato)
$Ph_2P^1(C_7H_5N^1)(C_3H_6)N^2(C_7H_5O_2)$	(N-(2-((2-(diphenylphosphino)benzylidene)amino)
	propyl)-2-hydroxybenzamidato)
$Ph_2P^1(C_7H_5N^1)(C_5H_7O)N^2(C_{10}H_{10}N_2)$	R7C-(N-(5,7-(dimethyl-1,8-naphtylridin-2-yl)-N ² -
	(2-(diphenylphosphinyl)benzylidene) valinamidato)
$Ph_2P^1(C_7H_5N^1)(C_6H_4)N^2(C_{10}H_9NO_3)$	(N ² -benzyloxycarbinol)-N-(2-(((2-(diphenylphosphanyl)
	phenyl)methylidene) amino)phenyl)glycinamide)
$Ph_2P^1(C_7H_5N^1)(C_7H_8C^1)(C_7H_8N^2)$	(2-(1b)-1-(((2-diphenylphosphinobenzylidene)amine)
	ethyl)phenyl)
$Ph_2P^1(C_7H_5N^1)(MeS^1)(Bu^tNH_2)$	(N-{N-[2-(diphenylphosphino)benzylidene)]-}
	{D/L-methionyl}-terc-butylamine
$Ph_2P^1(C_7H_5N^1)(NC_5H_4N^2)$	(2-(2-(diphenylphosphino)benzylidene)-1-
	(pyridine-2-yl)diazanido
$Ph_2P^1(C_7H_5N^1C_3H_6Se^1(Ph))$	(N-(2-(diphenylphosphino)benzylidene)-N-
	(3-(phenylseleno)propyl)amine
$Ph_2P^1(C_7H_5N^1O^1)$	(2-diphenylphosphino)-2-aminobenzaldehyde)
$Ph_2P^1(C_7H_6N^1)(C_7H_8N)(C_7H_8N^2)$	(N ² -(2-(diphenylphosphino)benzyl)-N,N-bis
	(2-pyridyl-2-ethyl)amine)
$Ph_2P^1(C_7H_6N^1)(NC_7H_5O^1)Ph_2P^2(C_{15}H_{13}N_2O)$	(N-(2-(diphenylphosphino)-1-phenylformyl)
	benzohydiazino)-N-(2-(diphenylphosphino)-1-
	phenylvinyl)benzohydeazone)
$Ph_2P^1(C_7H_6N^1 = NCC^1C_5H_6)$	(2-((2-(diphenylphosphino)-4-methylphenyl)diazinyl)-

5-methylphenyl)pyridine

pyridine

triclinic

phenyl)phosphino)benzenethiazato)

(2-(((2-(isopropysulfanyl)phenyl)(2-isopropylsulfanyl)

 $Pr^{i}S^{1}(C_{6}H_{4})P^{1}(C_{6}H_{4}SPr^{i}).(C_{6}H_{4})S^{2})$

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