

Structural Aspects of $\text{Pt}(\eta^3\text{-P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2)(\text{Y})$ Derivative Types

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Abstract: In this structural study, structural data are classified and analyzed for almost seventy complexes of the general formula $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$ ($\text{X}^1 = \text{O}, \text{N}, \text{C}, \text{S}, \text{Si}$) and ($\text{Y} =$ various monodentate ligands), in which the respective $\eta^3\text{-P}^1\text{X}^1\text{P}^2$ ligand forms a pair of five-membered metallocyclic rings with a common X^1 atom of the $\text{P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2$ type. The present complexes crystallize in five crystal systems: trigonal ($1\times$), tetragonal ($1\times$), orthorhombic ($11\times$), triclinic ($18\times$), and monoclinic ($39\times$). In 69 complexes, a η^3 ligand with monodentate Y constructs a distorted square planar geometry around each $\text{Pt}(\text{II})$ atom. There is only one complex in which $\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{P}^3\text{Ph}_3)$ constructs a trigonal-pyramidal geometry around a $\text{Pt}(\text{II})$ atom. The three P atoms construct a trigonal plane, and the Si atom occupies a pyramid. The structural data are discussed from various points of view, including the covalent radii of the atoms, the degree of distortion, and *trans*-influence. The *trans*-effect on the Pt-L bond distance also affects the L-PT-L bond angles, as well as the distortion of square planar geometry around $\text{Pt}(\text{II})$ atoms.

Keywords: structure; heterotridentate; $\text{Pt}(\eta^3\text{-P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2)(\text{Y})$; *trans*-influence; review



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1. Introduction

The chemistry of platinum coordination complexes has been intensively studied and developed for more than five decades, focusing on the relationship between structure and reactivity. The chemistry of platinum is important in the fields of biochemistry [1], catalysis [2], spectroscopy [3,4], and coordination theory. Very recently, Horiuchi and Umakoshi published a review that focused on the importance of and advances in the synthetic, structural, thermodynamic, electronic, and photophysical properties of Pt-based heteropolynuclear complexes [5].

Significant attention has been paid to organomonophosphines, representing soft donor ligands in the chemistry of platinum. There are a large number of published structural studies on such complexes that have been classified and analyzed [6]. Another group of related structural studies is devoted to $\text{Pt}(\text{II})$ complexes with organodiphosphines [7,8]. Recently, we analyzed and classified structural data for the following compositions: $\text{Pt}(\eta^4\text{-P}_4\text{L})$, $\text{Pt}(\eta^4\text{-P}_3\text{SiL})$, $\text{Pt}(\eta^4\text{-P}_2\text{N}_2\text{L})$, $\text{Pt}(\eta^4\text{-P}_2\text{S}_2\text{L})$, $\text{Pt}(\eta^4\text{-P}_2\text{C}_2\text{L})$, $\text{Pt}(\eta^4\text{-PN}_3\text{L})$, and $\text{Pt}(\eta^4\text{-PN}_2\text{OL})$ [9]. As can be seen, P-donor ligands prevail by far. η^4 -ligands form 10-, 11-, 12-, 14-, and 16-membered metallocycles. A distorted square planar geometry around $\text{Pt}(\text{II})$ atoms with cis-configuration prevails by far.

From an application point of view, multifunctional ligands responsible for secondary catalyst–substrate interactions over the course of a catalytic transformation play increasingly important roles in contemporary catalysis, as has been demonstrated also within

these groups of platinum complexes with P-donor ligands. Pincer-type complexes constitute a family of compounds that have recently attracted significant interest. They play important roles in organometallic reactions and mechanisms, catalysis, and the design of new materials (see, e.g., reviews [10–16]). The high thermal stability of such complexes, particularly those based on an aromatic backbone, permits their use as catalysts at elevated temperatures in various catalytic applications. Bulky bis-chelating pincer-type ligands are effective in the stabilization of highly unsaturated cationic complexes and the stabilization of reactive species [10–17].

As a continuation of the investigation of platinum complexes with P-donor ligands, this structural study aims to classify and analyze the structural parameters of heterotridentate organodiphosphines in monomeric four-coordinated platinum complexes of the $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{O}^1\text{L}$, N^1L , C^1L , S^1L , or Si^1L) type, in which each tridentate ligand creates a pair of “equal” five-membered rings with a common X^1 atom of the $\text{P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2$ type. The application potentialities of these ligands and their complexes are reviewed, as well, to demonstrate the prevailing areas of their practical use.

2. $\text{Pt}(\eta^3\text{-P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{O}^1, \text{N}^1, \text{C}^1, \text{S}^1$, or Si^1)

There are 69 complexes in which heterotridentate organodiphosphines create a pair of “equal” five-membered metallocyclic rings with a common X^1 atom. These tridentate ligands with monodentate Y ligands construct a square planar geometry with various degrees of distortion around Pt(II) atoms. These complexes are centrosymmetric. Groups of $\text{X}^1 = \text{O}^1$, N^1 , or C^1 structures, which were mentioned for several representatives in our previous work devoted to any type of n-member metallocycle rings ($n = 5, 6, 7$) but different types of atoms between P^1 and X^1 [18], are analyzed in detail in this work, along with a new group of $\text{X}^1 = \text{S}^1$, Si^1 structures, highlighting structural aspects related to distortion. The complexes are described in detail via the relevant structural data gathered in Tables 1–3 for $\text{Pt}\{\eta^3\text{-P}^1\text{X}^1\text{P}^2\}(\text{Y})$, ($\text{X}^1 = \text{O}^1, \text{N}^1$), ($\text{Y} = \text{C}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{P}^3\text{L}$); $\text{Pt}\{\eta^3\text{-P}^1\text{C}^1\text{P}^2\}(\text{Y})$, ($\text{Y} = \text{O}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{Br}$); and $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{S}^1$ or Si^1), ($\text{Y} = \text{C}^2\text{L}, \text{Cl}, \text{P}^3\text{L}, \text{I}, \text{H}, \text{O}^2\text{L}$) structural subgroups, respectively. The chemical structures of particular complexes in these subgroups are gathered in Supplementary Materials and Tables S1–S3 therein. The majority of the cited works describe the synthesis and structural characterization of various ligands and their Pt(II) complexes (just one example of a square planar Pt(0) complex). Pincer ligands and their Pt(II) complexes dominate in the presented application examples; they are all focused on various aspects of synthesis and catalysis performance, as can be seen from brief summaries in Tables S1–S3.

Table 1. Crystallographic and structural data for $\text{Pt}\{\eta^3\text{-P}^1\text{X}^1\text{P}^2\}(\text{Y})$, ($\text{X}^1 = \text{O}^1, \text{N}^1$), ($\text{Y} = \text{C}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{P}^3\text{L}$) complexes ^a.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{15}\text{H}_{12}\text{O})\text{PPh}_2\}\{\eta^1\text{-P}^3(\text{C}_5\text{H}_4\text{N})(\text{Ph})_2\}]\cdot 2\text{CF}_3\text{SO}_3\cdot 0.5\text{H}_2\text{O}$ (at 150 K)	m C2/c 4	42.762(0) 12.161(0) 23.995(0)	121.60(0)	PtP_2OP ($\text{P}^1\text{C}_2\text{O}^1\text{C}_2\text{P}^2$) 0.164	P^1, P^2 2.302(-,11) O ¹ 2.189 P ³ 2.239	$\text{P}^{1,2}, \text{O}^1$ 81.6(-,7) ^d P ¹ , P ² 162.2 P ^{1,2} , P ³ 98.5(-,1,7) O ¹ , P ³ 174.7(2)	[19]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{12}\text{H}_8\text{N})\cdot \text{PPh}_2\text{-P}^1, \text{N}^1, \text{P}^2\}(\text{py})]\cdot \text{CF}_3\text{SO}_3\cdot \text{toluene}$	m P2 ₁ /n 4	15.114(0) 17.695(0) 16.901(0)	105.98(0)	PtP_2NN ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.125	P ¹ 2.294 P ² 2.273 N ¹ 2.024 py, N ² 2.056	P ^{1,2} , N ¹ 83.3(-,7) ^d P ¹ , P ² 166.6 P ^{1,2} , N ² 96.1(-,3.0) N ¹ , N ² 175.6	[20]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_2\text{H}_8\text{N})\text{PPh}_2\text{-P}^1, \text{N}^1, \text{P}^2\}(\text{CH}_3)]$	or Fdd2 4	9.961(0) 18.601(0) 32.725(0)		PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.110	P ¹ 2.274 P ² 2.274 N ¹ 2.093 C 2.110	P ^{1,2} , N ¹ 82.3 ^d P ¹ , P ² 164.6 P ^{1,2} , C 97.7 N ¹ , C 180.0	[20]
$[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{P}^1, \text{N}^1, \text{P}^2\}(\text{CH}_3)]\text{Cl}\cdot \text{CHCl}_3$ (at 100 K)	tr P1 2	14.569(0) 15.447(0) 16.237(0)	114.73(0) 99.12(0) 96.40(0)	PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.128	P ¹ 2.286 P ² 2.301 N ¹ 2.108 C 2.057	P ^{1,2} , N ¹ 84.0 ^d P ¹ , P ² 164.4 P ^{1,2} , C 96.1(-,1) N ¹ , C 177.5	[21]
$[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{P}^1, \text{N}^1, \text{P}^2\}(\text{CH}_3)]\text{Cl}\cdot \text{CHCl}_3$ (at 100 K)	m P2 ₁ /c 8	10.976(2) 15.479(3) 30.094(3)	90.71(3)	PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.120	P ¹ 2.295 P ² 2.282 N ¹ 2.089 C 2.105	P ^{1,2} , N ¹ 83.2(-,4) ^d P ¹ , P ² 164.6 N ¹ , N ² 96.6(-,5) N ¹ , C 178.3	[21]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{P}^1, \text{N}^1, \text{P}^2\}(\text{C}=\text{O})\text{Et}]\cdot \text{BF}_4\cdot 0.5\text{CH}_2\text{Cl}_2$ (at 100 K)	m P2 ₁ /n 4	18.173(3) 9.960(1) 21.092(4)	114.94(0)	PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.130	P ¹ 2.279 P ² 2.284 N ¹ 2.131 C 2.001	P ^{1,2} , N ¹ 81.8(-,4) ^d P ¹ , P ² 163.6 P ^{1,2} , C 98.1(-,1.8) N ¹ , C 178.0	[22]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{P}^1, \text{N}^1, \text{P}^2\}(\text{CH}_2\text{CHO})]\cdot \text{BF}_4$ (at 110 K)	tr P1 2	9.198(1) 10.688(1) 16.421(1)	99.77(0) 100.04(0) 97.95(0)	PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.112	P ¹ 2.269 P ² 2.303 N ¹ 2.112 C 2.132	P ^{1,2} , N ¹ 83.0(-,2) ^d P ¹ , P ² 165.9 P ^{1,2} , C 97.0(-,1.7) N ¹ , C 178.1	[22]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{P}^1, \text{N}^1, \text{P}^2\}(\text{CH}=\text{CHPh})]\cdot \text{BF}_4$	tr P1 2	12.534(8) 17.101(8) 17.919(8)	70.04(0) 82.64(0) 78.66(0)	PtP_2NC ($\text{P}^1\text{C}_2\text{N}^1\text{C}_2\text{P}^2$) 0.135	P ¹ 2.289 P ² 2.309 N ¹ 2.125 C 2.005	P ^{1,2} , N ¹ 82.3(-,6) ^d P ¹ , P ² 164.3 P ^{1,2} , C 97.6(-,1.2) N ¹ , C 176.6	[23]

Table 1. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt{ η^3 -Pr ⁱ ₂ P(C ₁₂ H ₇ F ₂ N)PPr ⁱ ₂ -P ¹ ,N ¹ ,P ² }(C ₆ H ₄ F)].B(C ₆ F ₄) ₄ (at 110 K)	m P2 ₁ /c 4	15.495(2) 18.673(3) 22.444(2)	125.95(0)	PtP ₂ NC (P ¹ C ₂ N ¹ C ₂ P ²) 0.171	P ¹ 2.286 P ² 2.272 N ¹ 2.126 C 2.015	P ^{1,2} ,N ¹ 83.0(-,1.2) P ¹ ,P ² 163.4 P ^{1,2} ,C 96.5(-,2.0) N ¹ ,C 172.3	[24]
[Pt{ η^3 -Pr ⁱ ₂ P(C ₁₂ H ₇ F ₂ N)PPr ⁱ ₂ -P ¹ ,N ¹ ,P ² }(p-tol)].B(C ₆ F ₅) ₄ (at 110 K)	m P2 ₁ /n 4	15.655(1) 18.868(1) 18.242(1)	98.76(0)	PtP ₂ NC (P ¹ C ₂ N ¹ C ₂ P ²) 0.225	P ¹ 2.288 P ² 2.270 N ¹ 2.183 C 2.070	P ^{1,2} ,N ¹ 83.9(-,8) P ¹ ,P ² 161.4 P ^{1,2} ,C 97.4(-,3.5) N ¹ ,C 166.8	[24]
[Pt{ η^3 -Ph ₂ P(C ₇ H ₇ N)PPh ₂ -P ¹ ,N ¹ ,P ² }(C ₁₁ H ₁₅ O ₃)].BF ₄	m P2 ₁ /c 4	18.286(2) 11.617(3) 20.683(1)	114.68(1)	PtP ₂ NC (P ¹ C ₂ N ¹ C ₂ P ²) 0.130	P ¹ 2.263 P ² 2.282 N ¹ 2.097 C 2.157	P ^{1,2} ,N ¹ 83.0(-,9) P ¹ ,P ² 164.9 P ^{1,2} ,C 97.1(-,1.6) N ¹ ,C 176.6	[25]
[Pt{ η^3 -Ph ₂ P(C ₁₂ H ₈ N)PPh ₂ }(Cl)].5C ₆ H ₆	m P2 ₁ /n 4	17.378(0) 12.705(0) 25.555(0)	104.58(0)	PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.107	P ^{1,2} 2.277(-,7) N ¹ 2.024 Cl 2.318	P ^{1,2} ,N ¹ 83.7(-,1) P ¹ ,P ² 167.3 P ^{1,2} ,Cl 96.3(-,1.9) N ¹ ,Cl 177.5	[20]
[Pt{ η^3 -Bu ^t ₂ P(C ₇ H ₆ N)PBU ^t ₂ }(Cl)]	or Pna2 ₁ 4	22.499(0) 8.107(0) 14.161(0)		PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.102	P ^{1,2} 2.296(-,15) N ¹ 2.021 Cl 2.333	P ^{1,2} ,N ¹ 84.6(-,3) P ¹ ,P ² 169.2 P ^{1,2} ,Cl 95.3(-,4) N ¹ ,Cl 176.5	[21]
[Pt{ η^3 -Bu ^t ₂ P(C ₇ H ₇ N)PBU ^t ₂ }(Cl)]Cl	trg P3 6	18.631(3) 14.821(3)		PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.092	P ^{1,2} 2.302(-,1) N ¹ 2.030 Cl 2.307	P ^{1,2} ,N ¹ 84.2(-,3) P ¹ ,P ² 168.2 P ^{1,2} ,Cl 95.8(-,5) N ¹ ,Cl 178.9	[21]
[Pt{ η^3 -Pr ⁱ ₂ P(C ₁₂ H ₆ F ₂ N)PPr ⁱ ₂ }(Cl)].CHB ₁₁ Cl ₁₁ (at 110 K)	m P2 ₁ /c 4	19.446(20) 15.820(18) 15.256(15)	107.78(1)	PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.151	P ¹ 2.285 P ² 2.304 N ¹ 1.987 Cl 2.297	P ^{1,2} ,N ¹ 84.2(-,6) P ¹ ,P ² 166.7 P ^{1,2} ,Cl 95.8(-,1.9) N ¹ ,Cl 171.9	[24]
[Pt{ η^3 -Ph ₂ P(C ₁₄ H ₁₂ N)PPr ⁱ ₂ }(Cl)].0.5C ₆ H ₆ (at 183 K)	m P2 ₁ /c 4	9.702(0) 11.526(0) 28.499(1)	100.73(0)	PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.120	P ^{1,2} 2.278(-,5) N ¹ 2.028 Cl 2.321	P ^{1,2} ,N ¹ 83.2(-,1.2) ^d P ¹ ,P ² 164.0 P ^{1,2} ,Cl 96.7(-,1.2) N ¹ ,Cl 179.2	[26]

Table 1. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt{ η^3 -Ph ₂ P(C ₁₄ H ₁₂ N) P(cy) ₂ } (Cl)].C ₆ H ₆ (at 183 K)	tr P $\bar{1}$ 2	11.322(0) 11.735(0) 15.501(0)	93.81(0) 110.18(0) 93.00(0)	PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.135	P ^{1,2} 2.282(-,9) N ¹ 2.047 Cl 2.322	P ^{1,2} ,N ¹ 82.9(-,1) P ¹ ,P ² 164.8 P ^{1,2} ,Cl 97.2(-,2.0) N ¹ ,Cl 176.1	[26]
[Pt{ η^3 -Ph ₂ P(CH ₂)(C ₅ H ₄ N)(CH ₂)Ph ₂ P- P ¹ ,N ¹ ,P ² }(Cl)]	m P2 ₁ /n 4	15.915(5) 19.337(8) 8.861(6)	98.94(2)	PtP ₂ NCl (P ¹ C ₂ N ¹ C ₂ P ²) 0.089	P ^{1,2} 2.285(3,1) N ¹ 2.2008(7) Cl 2.312(3)	P ^{1,2} ,N ¹ 84.6(2,4) ^d P ¹ ,P ² 169.0(2) P ^{1,2} ,Cl 95.5(1,9) N ¹ ,Cl 178.5(2)	[27]
[Pt{ η^3 -(η^1 -C ₂₄ H ₄₄)P(C ₇ H ₆ N)P(η^1 - C ₂₄ H ₄₄)}(PPh ₃)].2CH ₂ Cl ₂ (at 103 K)	tr P $\bar{1}$ 2	13.341(2) 18.981(4) 30.668(6)	93.86(0) 90.89(0) 98.03 (0)	PtP ₂ NP (P ¹ C ₂ N ¹ C ₂ P ²) 0.199	P ^{1,2} 2.317(-,8) N ¹ 2.082(3) P ₃ 2.270	P ^{1,2} ,N ¹ 80.9(-,6) ^d P ¹ ,P ² 158.7 P ^{1,2} ,P ³ 98.3(-,2.0) N ¹ ,P ³ 173.0	[28]
[Pt{ η^3 -(η^2 -C ₁₈ H ₂₈)P(C ₇ H ₆ N)P(η^1 - C ₁₈ H ₂₉)}(Pcy ₃)] (at 103 K)	m P2 ₁ /c 4	17.281(2) 11.881(1) 28.514(4)	104.32(0)	PtP ₂ NP (P ¹ C ₂ N ¹ C ₂ P ²) 0.209	P ¹ 2.326 P ² 2.389 N ¹ 2.073 P ₃ 2.284	P ^{1,2} ,N ¹ 82.7(-,1.1) ^d P ² ,N ¹ 162.9 P ¹ ,P ¹ 98.0(-,5.8) N ¹ ,P ³ 167.5	[29]

Footnotes: a—Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is e.s.d., and the second is the maximum deviation from the mean. b—The parameters, τ_4 , were calculated: $\tau_4 = 360 - (\alpha + \beta)/141$, where β and α are the two largest angles and assume the values of 0 and 1 for the perfect square planar and perfect tetrahedral geometries, respectively. c—The chemical identity of the coordinated atom or ligand is specified in these columns. d—The five-membered metallocyclic ring.

Table 2. Crystallographic and structural data for $\text{Pt}\{\eta^3\text{-P}^1\text{C}^1\text{P}^2\}(\text{Y})$, ($\text{Y} = \text{O}^2\text{L}, \text{N}^2\text{L}, \text{CL}, \text{Cl}, \text{Br}$) complexes ^a.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
$[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P(C}_8\text{H}_7\text{)P(CF}_3)_2\}.$ $(\text{H}_2\text{O})\text{]SbF}_6$ (at 150 K)	m C2/c 4	41.924(0) 10.457(0) 22.512(0)	110.54(0)	PtP_2CO $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.143	$\text{P}^{1,2}$ 2.245 C^1 1.995 H_2O 2.156	$\text{P}^{1,2}, \text{C}^1$ 81.7(-,2) ^d P^1, P^2 163.3 $\text{P}^{1,2}, \text{O}$ 98.3(-,3.9) C^1, O 176.3	[30]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_8\text{H}_7\text{)PPh}_2\}(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3$ (at 165 K)	tr Pi 2	9.644(1) 13.885(1) 14.012(3)	119.08(1) 93.43(1) 104.59(1)	PtP_2CO $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.146	$\text{P}^{1,2}$ 2.295(-,3) C^1 1.995 H_2O 2.156	$\text{P}^{1,2}, \text{C}^1$ 82.0(-,6) ^d P^1, P^2 163.7 $\text{P}^{1,2}, \text{O}$ 98.1(-,2.7) C^1, O 176.6	[31]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_8\text{H}_7\text{)PPh}_2\}(\text{OMe})].0.5\text{C}_6\text{H}_6$	tr Pi 2	8.824(2) 12.517(1) 14.712(2)	91.94(1) 104.96(1) 104.20(1)	PtP_2CO $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.120	$\text{P}^{1,2}$ 2.266(-,4) C^1 2.053 MeO 2.086	$\text{P}^{1,2}, \text{C}^1$ 83.7(-,7) ^d P^1, P^2 166.6 $\text{P}^{1,2}, \text{O}$ 98.8(-,6.8) C^1, O 176.5	[31]
$[\text{Pt}\{(\eta^3\text{-Pr}^i_2)\text{P(C}_{20}\text{H}_{11})\text{P(Pr}^i_2)\}(\text{OOC CF}_3)]$ (at 173 K)	or Fdd2 4	29.241(1) 39.275(2) 11.361(0)		PtP_2CO $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.181	$\text{P}^{1,2}$ 2.289(-,1) C^1 2.045 O 2.139	$\text{P}^{1,2}, \text{C}^1$ 85.8(-,1) ^d P^1, P^2 157.0 $\text{P}^{1,2}, \text{O}$ 94.2(-,2.5) C^1, O 177.4	[32]
$[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P(C}_8\text{H}_7\text{)P(CF}_3)_2\}(\text{NC}_5\text{F}_5)]\text{B(C}_6\text{F}_5)_4$ (at 150 K)	m P2 ₁ /c 4	13.932(1) 17.137(2) 19.213(0)	96.29(0)	PtP_2CN $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.138	$\text{P}^{1,2}$ 2.242(-,2) C^1 2.030 N 2.173	$\text{P}^{1,2}, \text{C}^1$ 80.6(-,1) ^d P^1, P^2 161.3 $\text{P}^{1,2}, \text{N}$ 99.3(-,5) C^1, N 179.2	[30]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_{20}\text{H}_{13}\text{O}_4\text{)PPh}_2\}.$ $(\text{N}\equiv\text{CCH}_3)]\text{BF}_4$ (at 173 K)	or Pca21 6	21.587(3) 8.904(1) 21.327(3)		PtP_2CN $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.191	$\text{P}^{1,2}$ 2.303(-,1) C^1 1.892 N 2.088	$\text{P}^{1,2}, \text{C}^1$ 85.9(-,1.9) ^d P^1, P^2 156.4 $\text{P}^{1,2}, \text{N}$ 93.5 C^1, N 176.8	[32]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_{20}\text{H}_{11}\text{O}_2\text{)PPh}_2\}.$ $(\text{NC}_5\text{H}_5)]\text{Cl}(\text{NC}_5\text{H}_5)_3$	m P2 ₁ /c 4	12.892(6) 15.613(8) 26.900(10)	101.48(1)	PtP_2CN $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.138	$\text{P}^{1,2}$ 2.275(-,2) C^1 2.021 N 2.111	$\text{P}^{1,2}, \text{C}^1$ 81.0 ^d P^1, P^2 162.0 $\text{P}^{1,2}, \text{N}$ 98.8 C^1, N 178.5	[33]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_{20}\text{H}_{11}\text{O}_2\text{)PPh}_2\}.$ $(\text{N}\equiv\text{CCH}_3)]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$ (at 173 K)	m P2 ₁ /c 4	14.711(1) 15.920(1) 17.987(1)	92.15(0)	PtP_2CN $(\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2)$ 0.202	$\text{P}^{1,2}$ 2.293(-,5) C^1 2.062 N 2.056	$\text{P}^{1,2}, \text{C}^1$ 85.7(-,3) ^d P^1, P^2 157.4 $\text{P}^{1,2}, \text{N}$ 97.3(-,3) C^1, N 174.0	[33]

Table 2. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -Ph ₂ P(C ₂₄ H ₁₉ O ₂)PPh ₂)(CN)] (at 103 K)	tg P2 ₁ 2 ₁ 2 ₁ 4	9.492(0) 9.492 (0) 13.030(1)		PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.140	P ^{1,2} 2.286 C ¹ 2.029 NC 2.062	P ^{1,2} ,C ¹ 80.1 ^d P ¹ ,P ² 160.1 P ^{1,2} ,C 99.2 C ¹ ,C 180.0	[34]
[Pt(η^3 -(CF ₃) ₂ P(C ₈ H ₇)P. (CF ₃) ₂)(CO)]SbF ₆	tr P1 2	11.770(1) 13.950(1) 14.529(1)	91.31(0) 100.81(0) 91.90(0)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.125	P ^{1,2} 2.256 C ¹ 1.969 OC 2.053	P ^{1,2} ,C ¹ 81.6(-,3) ^d P ¹ ,P ² 163.4 P ^{1,2} ,C 98.3(-,3) C ¹ ,C 179.0	[35]
[Pt(η^3 -(CF ₃) ₂ P(C ₈ H ₇)P. (CF ₃) ₂)(CH ₃)]	m P2 ₁ /c 8	14.732(0) 16.189(0) 17.737(0)	113.42(3)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.153	P ^{1,2} 2.203(-,2) C ¹ 2.089 H ₃ C 2.148	P ^{1,2} ,C ¹ 81.0(-,5) ^d P ¹ ,P ² 161.0 P ^{1,2} ,C 98.9(-,4) C ¹ ,C 177.3	[35]
[Pt(η^3 -Pr ⁱ ₂ P(C ₈ H ₇)PP ⁱ ₂)(CO)]. CF ₃ SO ₃ 0.5C ₆ H ₆ (at 120 K)	m P2 ₁ /c 4	13.430(3) 15.667(3) 15.472(3)	112.73(3)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.117	P ^{1,2} 2.305(-,2) C ¹ 2.048 C 2.053	P ^{1,2} ,C ¹ 82.7(-,5) ^d P ¹ ,P ² 165.2 P ^{1,2} ,C 97.3(-,9) C ¹ ,C 178.2	[36]
[Pt(η^3 -Bu ^t ₂ P(C ₈ H ₇)PBu ^t ₂)(η^1 - CHOMe)].CF ₃ SO ₃ .thf (at 120 K)	m P2 ₁ /c 4	15.824(0) 11.375(0) 20.093(0)	97.46(0)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.123	P ^{1,2} 2.302(-,1) C ¹ 2.081 C 1.986	P ^{1,2} ,C ¹ 81.9(-,3) ^d P ¹ ,P ² 163.5 P ^{1,2} ,C 98.0(-,1.1) C ¹ ,C 179.2	[34]
[Pt(η^3 -Bu ^t ₂ P(C ₁₂ H ₉)PBu ^t ₂) (CO)]BF ₄ (at 120 K)	or Pna2 ₁ 8	12.097(2) 13.150(3) 38.514(8)		PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.102	P ^{1,2} 2.311(-,4) C ¹ 2.074 OC 1.903	P ^{1,2} ,C ¹ 83.1(-,1) ^d P ¹ ,P ² 166.3 P ^{1,2} ,C 96.8(-,2) C ¹ ,C 179.3	[37]
[Pt(η^3 -Ph ₂ P(C ₈ H ₇)PPh ₂)(η^1 -C ₁₂ H ₁₉ N ₂)] (at 150 K)	m P2 ₁ /c 4	17.576(3) 12.436(2) 18.593(5)	114.34(1)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.146	P ^{1,2} 2.269(-,2) C ¹ 2.142 C 2.091	P ^{1,2} ,C ¹ 81.0(-,2) ^d P ¹ ,P ² 162.0 P ^{1,2} ,C 99.0(-,3.1) C ¹ ,C 177.5	[38]
[Pt(η^3 -Ph ₂ P(C ₈ H ₇)PPh ₂)(η^1 -C ₃ F ₇)] (at 150 K)	m P2 ₁ /c 4	10.192(3) 18.106(8) 17.018(3)	91.01(1)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.143	P ^{1,2} 2.279(-,2) C ¹ 2.072 C 2.186	P ^{1,2} ,C ¹ 81.4(-,2) ^d P ¹ ,P ² 162.8 P ^{1,2} ,C 98.4(-,5) C ¹ ,C 177.0	[39]

Table 2. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -Ph ₂ P(C ₈ H ₇)PPh ₂) (η^1 -C ₁₂ H ₂₁ N ₂)]2BF ₄ (at 150 K)	m C2 2	12.887(0) 15.901(0) 12.177(0)	121.54(0)	PtP ₂ C ₂ (P ¹ C ₂ C ¹ C ₂ P ²) 0.133	P ^{1,2} 2.275 C ¹ 2.084 C 2.096	P ^{1,2} ,C ¹ 80.6 ^d P ¹ ,P ² 161.2 P ^{1,2} ,C 99.4 C ¹ ,C 180.0	[40]
[Pt(η^3 -Ph ₂ P(C ₂₀ H ₁₁ O ₂ P)Ph ₂)Cl]. (CH ₃ CN) ₄ (at 150 K)	tr Pi 2	12.485(1) 14.669(2) 15.038(2)	118.03(0) 106.22 (0) 90.30(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.232	P ^{1,2} 2.265 C ¹ 2.086 Cl 2.394	P ^{1,2} ,C ¹ 85.4(-,3) ^d P ¹ , P ² 155.4 P ^{1,2} ,Cl 96.2(-,6) C ¹ ,Cl 172.0	[33]
[Pt(η^3 -Ph ₂ P(C ₂₄ H ₁₉ O ₂)PPh ₂)Cl] (at 103 K)	m P2 ₁ 4	11.798(3) 26.540(2) 12.725(1)	96.64(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.138	P ^{1,2} 2.276(-,1) C ¹ 2.022 Cl 2.388	P ^{1,2} ,C ¹ 82.7(-,1.0) ^d P ¹ , P ² 163.9 P ^{1,2} ,Cl 97.4(-,4) C ¹ ,Cl 176.4	[34]
[Pt(η^3 -(CF ₃) ₂ P(C ₈ H ₇)P (CF ₃) ₂)Cl]1.5(C ₆ H ₆) (at 173 K)	m P2 ₁ /c 4	10.111(0) 19.270(0) 13.082(0)	102.86(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.156	P ^{1,2} 2.233(-,5) C ¹ 2.037 Cl 2.370	P ^{1,2} ,C ¹ 80.9(-,3) ^d P ¹ , P ² 161.0 P ^{1,2} ,Cl 99.2(-,5) C ¹ ,Cl 176.9	[35]
[Pt(η^3 -Bu ^t ₂ P(C ₈ H ₇)PBu ^t ₂)Cl] (at 120 K)	or P2 ₁ 2 ₁ 2 ₁ 8	12.965(3) 13.853(3) 14.642(3)		PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.094	P ^{1,2} 2.288(-,3) C ¹ 2.017 Cl 2.407	P ^{1,2} ,C ¹ 83.7(-,1) ^d P ¹ , P ² 167.3 P ^{1,2} ,Cl 96.3(-,64) C ¹ ,Cl 179.2	[36]
[Pt(η^3 -Bu ^t ₂ P(C ₁₂ H ₉)PBu ^t ₂)Cl] (at 120 K)	m P2 ₁ /n 4	16.195(3) 10.440(2) 17.588(4)	109.21(3)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.097	P ^{1,2} 2.287(-,6) C ¹ 2.016 Cl 2.431	P ^{1,2} ,C ¹ 83.9(-,4) ^d P ¹ , P ² 167.7 P ^{1,2} ,Cl 96.1(-,6) C ¹ ,Cl 178.7	[37]
[Pt(η^3 -Bu ^t ₂ P(C ₈ H ₇)PBu ^t ₂)Cl]	m P2 ₁ /n 4	12.018(0) 14.803(0) 15.728(0)	100.79(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.120	P ^{1,2} 2.305(-,3) C ¹ 2.065 Cl 2.434	P ^{1,2} ,C ¹ 83.8(-,5) ^d P ¹ , P ² 167.3 P ^{1,2} ,Cl 96.1(-,1) C ¹ ,Cl 175.6	[41]
Pt(η^3 -Pr ⁱ ₂ P(C ₈ H ₇)PPr ⁱ ₂)Cl] (at 120 K)	tr Pi 2	11.148(2) 13.935(3) 14.683(3)	78.16(3) 82.35(3) 89.33(3)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.105	P ^{1,2} 2.279(-,4) C ¹ 2.006 Cl 2.436	P ^{1,2} ,C ¹ 83.6(-,2) ^d P ¹ , P ² 167.4 P ^{1,2} ,Cl 96.1(-,1) C ¹ ,Cl 177.7	[42]

Table 2. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt{ η^3 -Ph ₂ P(C ₈ H ₇)PPh ₂ }Cl]	m P2 ₁ /n 4	10.290(2) 16.117(3) 15.173(3)	105.47(3)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.130	P ^{1,2} 2.277(-,2) C ¹ 2.002 Cl 2.383	P ^{1,2} ,C ¹ 81.6(-,6) ^d P ¹ ,P ² 163.1 P ^{1,2} ,Cl 98.4(-,1.1) C ¹ ,Cl 178.5	[43]
[Pt{ η^3 -Ph ₂ P(C ₁₄ H ₇)PPh ₂ }Cl]. CH ₃ CN (at 223 K)	m P2 ₁ /c 4	12.773(0) 17.780(0) 14.72448(0)	96.54(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.107	P ^{1,2} 2.268(-,2) C ¹ 1.991 Cl 2.391	P ^{1,2} ,C ¹ 83.7(-,1) ^d P ¹ ,P ² 167.3 P ^{1,2} ,Cl 96.2(-,1.7) C ¹ ,Cl 177.5	[44]
[Pt{ η^3 -Ph ₂ P(C ₁₃ H ₇ O ₂)PPh ₂ } Cl].CH ₃ CN (at 223 K)	or Pbca 8	18.768(0) 16.966(0) 21.649(0)		PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.138	P ^{1,2} 2.266(-,1) C ¹ 2.050 Cl 2.397	P ^{1,2} ,C ¹ 84.6(-,7) ^d P ¹ ,P ² 166.3 P ^{1,2} ,Cl 95.8(-,2) C ¹ ,Cl 174.3	[44]
[Pt{ η^3 -Ph ₂ P(C ₁₈ H ₁₉ O ₈) PPh ₂ }Cl]CH ₂ Cl ₂ (at 103 K)	or P2 ₁ 2 ₁ 2 ₁ 8	10.432(1) 17.092(2) 24.423(3)		PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.163	P ^{1,2} 2.277(-,5) C ¹ 2.006 Cl 2.385	P ^{1,2} ,C ¹ 81.0(-,1) ^d P ¹ ,P ² 162.0 P ^{1,2} ,Cl 99.0(-,5) C ¹ ,Cl 174.7	[45]
Pt{ η^3 -Pr ⁱ ₂ P(C ₂₀ H ₁₁)PPr ⁱ ₂ }Cl]. (CH ₃ CN) ₂	m P2 ₁ /n 4	14.622(0) 15.048(1) 15.642(1)	96.24(0)	PtP ₂ CCl (P ¹ C ₂ C ¹ C ₂ P ²) 0.171	P ^{1,2} 2.284(-,1) C ¹ 2.064 Cl 2.392	P ^{1,2} ,C ¹ 86.0(-,2) ^d P ¹ ,P ² 156.2 P ^{1,2} ,Cl 94.0(-,2) C ¹ ,Cl 179.53	[46]
[Pt{ η^3 -Ph ₂ P(C ₈ H ₇)PPh ₂ }Br]	m P2 ₁ /n 4	10.127(2) 14.776(2) 19.023(3)	91.01(1)	PtP ₂ CBr (P ¹ C ₂ C ¹ C ₂ P ²) 0.138	P ^{1,2} 2.272(-,14) C ¹ 2.023 Br 2.468	P ^{1,2} ,C ¹ 82.4(-,1) ^d P ¹ ,P ² 164.8 P ^{1,2} ,Br 97.7(-,6) C ¹ ,Br 175.8	[47]
[Pt{ η^3 -Bu ^t ₂ P(C ₆ H ₅ N ₂)PBU ^t ₂ }(Br)] (at 150 K)	m C2 4	15.517(0) 13.055(0) 15.383(0)	118.78(0)	PtP ₂ CBr (P ¹ C ₂ C ¹ C ₂ P ²) 0.140	P ¹ 2.290 P ² 2.030 Br 2.466	P ^{1,2} ,C ¹ 82.5 ^d P ¹ ,P ² 165.0 P ^{1,2} ,Br 97.5 C ¹ ,Br 175.2	[40]

Footnotes: a—Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is e.s.d., and the second is the maximum deviation from the mean. b—The parameters, τ_4 , were calculated $\tau_4 = 360 - (\alpha + \beta)/141$, where β and α are the two largest angles and assume the values of 0 and 1 for the perfect square planar and perfect tetrahedral geometries, respectively. c—The chemical identity of the coordinated atom or ligand is specified in these columns. d—Five-membered metallocyclic ring.

Table 3. Crystallographic and structural data for Pt(η^3 -P¹X¹P²)(Y), (X¹ = S¹ or Si¹), (Y = C²L, Cl, P³L, I, H, O²L) complexes ^a.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -Ph ₂ P(C ₆ H ₄)S(=O)(C ₆ H ₄)PPh ₂)(CH ₃)]PF ₆ ·CH ₃ CN (at 100 K)	m P2 ₁ /n 4	8.936(2) 16.722(4) 25.078(6)	95.72(1)	PtP ₂ SC (P ¹ C ₂ S ¹ C ₂ P ²) 0.102	P ^{1,2} 2.273(-,3) S ¹ 2.268 H ₃ C 2.093	P ^{1,2} ,S ¹ 86.6(-,1) ^d P ¹ ,P ² 167.0 P ^{1,2} ,C 93.2(-,3) S ¹ ,C 178.2 P ^{1,2} ,S 84.6 P ¹ ,P ² 162.7 P ^{1,2} ,Cl 94.8 S ¹ ,Cl 177.6 P ^{1,2} ,S ¹ 85.6 P ¹ ,P ² 164.4 P ^{1,2} ,Cl 95.8 S ¹ ,Cl 176.6	[48]
[Pt(η^3 -Ph ₂ P(C ₆ H ₄)S(=O)(C ₆ H ₄)PPh ₂)(Cl)].PF ₆ ·CH ₃ CN	m P2 ₁ /c 4	13.360(0) 15.308(0) 18.787(0)	106.11(0)	PtP ₂ SCl (P ¹ C ₂ S ¹ C ₂ P ²) 0.140	P ^{1,2} 2.307 S ¹ 2.192 Cl 2.316	P ^{1,2} ,S ¹ 86.0(-,3) ^d P ¹ ,P ² 162.4 P ^{1,2} ,P ³ 94.7 S ¹ ,P ³ 177.5 P ^{1,2} ,S ¹ 81.3 ^d P ¹ ,P ² 161.6 P ^{1,2} ,P ³ 98.7 S ¹ ,P ³ 178.3	[48]
[Pt(η^3 -Ph ₂ P(CH ₂) ₂ S(=O)(CH ₂) ₂ PPh ₂)(Cl)].ClO ₄	tr P $\bar{1}$ 2	9.460(2) 12.079(3) 13.834(3)	93.53(2) 103.85(2) 104.22(2)	PtP ₂ SCl (P ¹ C ₂ S ¹ C ₂ P ²) 0.135	P 2.319(2,0) S ¹ 2.182(2) Cl 2.318(1)	P ^{1,2} ,S ¹ 86.0(-,3) ^d P ¹ ,P ² 162.4 P ^{1,2} ,P ³ 94.7 S ¹ ,P ³ 177.5 P ^{1,2} ,S ¹ 81.3 ^d P ¹ ,P ² 161.6 P ^{1,2} ,P ³ 98.7 S ¹ ,P ³ 178.3	[49]
[Pt(η^3 -Ph ₂ P(C ₆ H ₄)S(=O)(C ₆ H ₄)PPh ₂)(PPh ₃)].0.5(CH ₂ Cl ₂)(at 100 K)	tr P $\bar{1}$ 2	11.295(5) 11.469(1) 17.269(1)	86.45(1) 88.54(1) 77.08(1)	PtP ₂ SP (P ¹ C ₂ S ¹ C ₂ P ²) 0.143	P ^{1,2} 2.273(-,3) S ¹ 2.313 Ph ₃ P ³ 2.281	P ^{1,2} ,S ¹ 86.0(-,3) ^d P ¹ ,P ² 162.4 P ^{1,2} ,P ³ 94.7 S ¹ ,P ³ 177.5 P ^{1,2} ,S ¹ 81.3 ^d P ¹ ,P ² 161.6 P ^{1,2} ,P ³ 98.7 S ¹ ,P ³ 178.3	[48]
[Pt(η^3 -Ph ₂ P(CH ₂) ₂ S(CH ₂) ₂)PPh ₂)(PPh ₃)].2.ClO ₄ Me ₂ CO (at 120 K)	or Pnma 4	15.698(3) 15.337(3) 19.957(4)		PtP ₂ SP (P ¹ C ₂ S ¹ C ₂ P ²) 0.143	P ^{1,2} 2.309(-,1) S ¹ 2.343 Ph ₃ P ³ 2.289	P ^{1,2} ,S ¹ 84.0(-,3) ^d P ¹ ,P ² 165.4 P ^{1,2} ,I 96.7 S, I 177.7	[50]
[Pt(η^3 -Ph ₂ P(C ₂₃ H ₂₈ S)PPh ₂)(I)](I).1.74 CH ₂ Cl ₂ (at 173 K)	tr P $\bar{1}$ 2	9.845(0) 15.277(0) 17.264(0)	84.94(0) 84.03(0) 89.18(0)	PtP ₂ Si (P ¹ C ₂ S ¹ C ₂ P ²) 0.120	P ^{1,2} 2.311(-,1) S ¹ 2.252 I 2.510	P ^{1,2} ,S ¹ 84.0(-,3) ^d P ¹ ,P ² 165.4 P ^{1,2} ,I 96.7 S, I 177.7	[51]
[Pt(η^3 -cyh ₂ P(C ₆ H ₄)Si(Me). (C ₆ H ₄)Pcyh ₂)(H)].0.5 pentane (at 150 K)	m C2/c 4	24.426(0) 16.300(0) 39.968(3)	105.39(0)	PtP ₂ SiH (P ¹ C ₂ Si ¹ C ₂ P ²) 0.179	P ^{1,2} 2.254(-,4) Si ¹ 2.326 H 1.486	P ^{1,2} ,Si ¹ 85.3(-,0) ^d P ¹ ,P ² 159.5 P ^{1,2} ,H 94.7(-,4,7) Si ¹ ,H 175.3	[52]
[Pt(η^3 -cyh ₂ P(C ₆ H ₄)Si(Me)(C ₆ H ₄)Pcyh ₂)(H)].1.25 pentane (at 93 K)	m C2/c 4	29.595(0) 17.388(0) 33.970(2)	99.64(0)	PtP ₂ SiH (P ¹ C ₂ Si ¹ C ₂ P ²) 0.158	P ^{1,2} 2.262(0,2) Si ¹ 2.336 H 1.527	P ^{1,2} ,Si ¹ 84.2(-,0) ^d P ¹ ,P ² 162.0 P ^{1,2} ,H 94.6(-,7) Si ¹ ,H 175.6	[52]

Table 3. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt{ η^3 -Ph ₂ P(C ₆ H ₄)Si(Me) (C ₆ H ₄)PPh ₂ }(OEt ₂)]·[B(C ₆ F ₅) ₃ (CH ₂ Ph)]·OEt ₂	tr P $\bar{1}$ 2	14.718(1) 14.957(1) 15.402(1)	100.40(0) 103.42(0) 99.60(0)	PtP ₂ SiO (P ¹ C ₂ Si ¹ C ₂ P ²) 0.115	P ^{1,2} 2.299(-,6) Si ¹ 2.276 O 2.282	P ^{1,2} , Si ¹ 83.9(-,1.0) ^d P ¹ , P ² 165.5 P ^{1,2} , O 96.1(-,2.3) Si ¹ , O 178.4	[53]
[Pt{ η^3 -cyh ₂ P(C ₆ H ₄)Si (Me)(C ₆ H ₄)Pcyh ₂ }(Ph)]·OEt ₂ (at 173 K)	tr P $\bar{1}$ 2	13.506(5) 14.057(5) 14.950(0)	116.38(0) 93.48(0) 112.52(0)	PtP ₂ SiC (P ¹ C ₂ Si ¹ C ₂ P ²) 0.156	P ^{1,2} 2.279(-,2) Si ¹ 2.324 C 2.139	P ^{1,2} , Si ¹ 83.7(-,1) ^d P ¹ , P ² 162.7 P ^{1,2} , C 96.8(-,2) Si ¹ , C 175.1	[53]
[Pt{ η^3 -Ph ₂ P(C ₆ H ₄)Si(Me)(C ₆ H ₄)PPh ₂ } (CH ₂ Ph)]·CH ₂ Cl ₂ (at 193 K)	tr P $\bar{1}$ 2	13.586(1) 16.908(1) 19.771(2)	89.73(0) 76.03(0) 67.88(0)	PtP ₂ SiC (P ¹ C ₂ Si ¹ C ₂ P ²) 0.151	P ^{1,2} 2.260 Si ¹ 2.356 C 2.201	P ^{1,2} , Si ¹ 82.6(-,3) ^d P ¹ , P ² 163.0 P ^{1,2} , C 97.0(-,1) Si ¹ , Cl 175.7	[53]
[Pt{ η^3 -Pr ⁱ ₂ P(C ₆ H ₄)Si(OH) (C ₆ H ₄)PPr ⁱ ₂ }(CO)]·B(C ₆ F ₅) ₄ (at 120 K)	tr P $\bar{1}$ 2	13.658(0) 15.098(0) 15.201(0)	112.54(0) 94.60(0) 116.83(0)	PtP ₂ SiC (P ¹ C ₂ Si ¹ C ₂ P ²) 0.179	P ^{1,2} 2.325(-,3) Si ¹ 2.365 OC 1.994	P ^{1,2} , Si ¹ 82.1(-,2) ^d P ¹ , P ² 161.2 P ^{1,2} , C 98.3(-,1.1) Si ¹ , C 173.4	[54]
[Pt{ η^3 -Pr ⁱ ₂ P(C ₆ H ₄)Si(H)(C ₆ H ₄)PPr ⁱ ₂ }(mes)] (at 110 K)	or P2 ₁ 2 ₁ 2 ₁ 6	8.186(0) 17.908(0) 21.795(1)		PtP ₂ SiC (P ¹ C ₂ Si ¹ C ₂ P ²) 0.171	P ^{1,2} 2.286(-,2) Si ¹ 2.312 C 2.154	P ^{1,2} , Si ¹ 83.4(-,2) ^d P ¹ , P ² 159.0 P ^{1,2} , C 98.4(-,1.1) Si ¹ , C 177.0	[55]
[Pt{ η^3 -Ph ₂ P(C ₆ H ₄)Si(Me)(C ₆ H ₄)PPh ₂ }(Cl)] (at 173 K)	m P4/c 4	9.911(1) 13.656(1) 23.845(3)	97.90(0)	PtP ₂ SiCl (P ¹ C ₂ Si ¹ C ₂ P ²) 0.250	P ^{1,2} 2.261 Si ¹ 2.278 Cl 2.437	P ^{1,2} , Si ¹ 84.9(-,6) ^d P ¹ , P ² 155.4 P ^{1,2} , Cl 97.0(-,1) Si ¹ , Cl 169.3	[53]
[Pt{ η^3 -Ph ₂ P(C ₆ H ₄)Si(Me)(C ₆ H ₄)PPh ₂ } (AlCl ₃)]·2(C ₆ H ₅ F) (at 193 K)	or P2 ₁ 2 ₁ 2 ₁ 4	16.111(1) 16.989(1) 17.437(1)		PtP ₂ SiCl (P ¹ C ₂ Si ¹ C ₂ P ²) 0.181	P ^{1,2} 2.289(-,0) Si ¹ 2.285 Cl 2.438	P ^{1,2} , Si ¹ 84.7(-,1) ^d P ¹ , P ² 164.2 P ^{1,2} , Cl 96.8(2,3) Si ¹ , Cl 170.2	[53]

Table 3. Cont.

Complex	Cryst. cl. Space gr. Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromophore (Chelate Rings) τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt{ η^3 -Pr ⁱ ₂ P(C ₆ H ₄)Si(OH)(C ₆ H ₄)PPr ⁱ ₂ }(Cl)] (at 120 K)	m P2 ₁ /c 4	8.465(0) 18.246(0) 16.810(0)	94.98(0)	PtP ₂ SiCl (P ¹ C ₂ Si ¹ C ₂ P ²) 0.163	P ^{1,2} 2.292(-,3) Si ¹ 2.277 Cl 2.469	P ^{1,2} , Si ¹ 84.2(-,1) ^d P ¹ , P ² 161.7 P ^{1,2} , Cl 96.3(-,1.2) Si ¹ , Cl 175.1	[54]
[Pt{ η^3 -Pr ⁱ ₂ P(C ₆ H ₄)Si(H)(C ₆ H ₄)Pcyh ₂ }(Cl)] (at 110 K)	m P2 ₁ /n 4	12.420(8) 13.735(8) 15.539(10)	99.74(0)	PtP ₂ SiCl (P ¹ C ₂ Si ¹ C ₂ P ²) 0.146	P ^{1,2} 2.296 Si ¹ 2.276 Cl 2.452	P ^{1,2} , Si ¹ 84.2(-,2) ^d P ¹ , P ² 162.4 P ^{1,2} , Cl 95.9(-,2.8) Si ¹ , Cl 177.1	[55]
[Pt{ η^3 -cyh ₂ P(C ₆ H ₄)Si(Me) (C ₆ H ₄)Pcyh ₂ }(Cl)] (at 153 K)	m P2 ₁ /c 4	13.104(3) 16.579(3) 17.770(4)	108.97(3)	PtP ₂ SiCl (P ¹ C ₂ Si ¹ C ₂ P ²) 0.140	P ^{1,2} 2.293 Si ¹ 2.279 Cl 2.460	P ^{1,2} , Si ¹ 84.7(-,1) ^d P ¹ , P ² 162.2 P ^{1,2} , Cl 95.4(-,1.8) Si ¹ , Cl 178.0	[56]

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—The parameters, τ_4 , were calculated $\tau_4 = 360 - (\alpha + \beta)/141$, where β and α are the two largest angles and assume the values of 0 and 1 for the perfect square planar and perfect tetrahedral geometries, respectively. c—The chemical identity of the coordinated atom or ligand is specified in these columns. d—Five-membered metallocyclic ring.

2.1. $Pt(\eta^3-P^1O^1P^2)(P^3)$

Monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_{15}H_{12}O)PPh_2\}\{\eta^1\text{-P}^3(C_5H_4N)(Ph)_2\}](CF_3SO_3)_2 \cdot 0.5H_2O$ [19] (at 150 K) is the only example of the $P^1C_2O^1C_2P^2$ metallocycle type. The structural data are summarized in Table 1. The chemical structure and practical application of this particular complex are presented in Table S1. The heterotridentate $\eta^3\text{-P}^1O^1P^2$ ligand with monodentate P^3L creates a distorted square planar geometry around a Pt(II) atom.

The total mean Pt–L bond distance elongates in the following sequences:

Pt ($\eta^3\text{-P}^1O^1P^2$)(Y), Y = P^3L (1 example): Pt–L: 2.189 (3) Å (O^1 , trans to P^3) < 2.239 (2) Å (P^3) < 2.302 (2,11) Å ($P^{1,2}$, mutually trans)

2.2. $Pt(\eta^3-P^1N^1P^2)(Y)$, (Y = N^2L , (x1), $CL(x9)$, $Cl(x7)$, $P^3L(x2)$)

There are nineteen examples of the $P^1C_2N^1C_2P^2$ metallocyclic type with a common N^1 atom, and their structural data are summarized in Table 1. The chemical structures and practical applications of these particular complexes are presented in Table S1. Monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_{12}H_8N)PPh_2\}(N^2C_5H_5)]CF_3SO_3 \cdot \text{toluene}$ [20] is the only example in which a N^2 donor ligand completed a square planar geometry around a Pt(II) atom ($PtP^1N^1P^2N^2$). The structure of $[Pt\{\eta^3\text{-Ph}_2P(C_{12}H_8N)PPh_2\}(N^2C_5H_5)]^+$ [20] is shown in Figure 1 as an example.

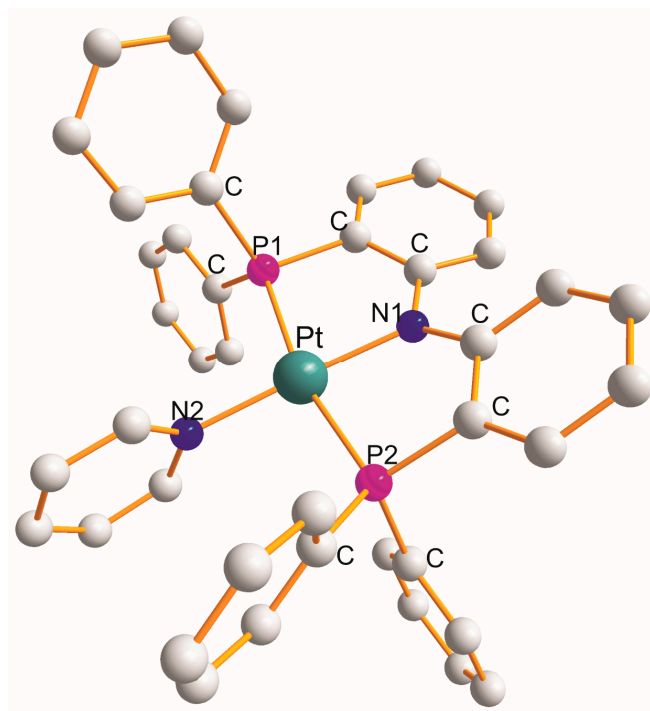


Figure 1. Structure of $[Pt\{\eta^3\text{-Ph}_2P(C_{12}H_8N)PPh_2\}(py)]$ [20].

In the following eight complexes, triclinic $[Pt\{\eta^3\text{-Bu}^t_2P(C_7H_7N)PBU^t_2\}(CH_3)]Cl$ (at 100 K), monoclinic $[Pt\{\eta^3\text{-Bu}^t_2P(C_7H_6N)PBU^t_2\}(CH_3)]$ [21] (at 100 K), monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_7H_7N)PPh_2\}[C(=O)Et]]BF_4 \cdot (CH_2Cl_2)_5$ [22] (at 100 K), triclinic $[Pt\{\eta^3\text{-Ph}_2P(C_7H_7N)PPh_2\}(CH_2CHO)]BF_4$ [22], triclinic $[Pt\{\eta^3\text{-Ph}_2P(C_7H_7N)PPh_2\}(CH=CHPh)]BF_4$ [23], monoclinic $[Pt\{\eta^3\text{-Pr}^{i2}P(C_{12}H_7F_2N)PPr^{i2}\}(C_6H_4F)]B(C_6H_5)_4$ (at 110 K) and monoclinic $[Pt\{\eta^3\text{-Pr}^{i2}P(C_{12}H_7F_2N)PPr^{i2}\} \cdot (p\text{-toluene})]B(C_6H_5)_4$ [24] (at 110 K), and monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_7H_7N)PPr^{i2}\}(\eta^1\text{-C}_{11}H_{15}NO_3)]BF_4$ [25] and a $\eta^3\text{-P}^1N^1P^2$ ligand with a monodentate CL create a distorted square planar geometry around a Pt(II) atom ($PtP^1N^1P^2C$).

There are seven complexes, monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_{12}H_8N)PPh_2\}(Cl)](C_6H_6)_5$ [20], trigonal $[Pt\{\eta^3\text{-Bu}^t_2P(C_7H_7N)PBU^t_2\}(Cl)]Cl$ [21], orthorhombic $[Pt\{\eta^3\text{-Bu}^t_2P(C_7H_6N)PBU^t_2\}(Cl)]$ [21] (at 120 K), monoclinic $[Pt\{\eta^3\text{-Pr}^{i2}P(C_{12}H_6F_2N)PPr^{i2}\}(Cl)]CHB_{11}Cl_{11}$ [24] (at 110 K), monoclinic $[Pt\{\eta^3\text{-Ph}_2P(C_{14}H_{12}N)PPr^{i2}\}(Cl)]C_6H_6$ [26] (at 183 K) and triclinic $[Pt\{\eta^3\text{-}$

$\text{Ph}_2\text{P}(\text{C}_{14}\text{H}_{12}\text{N})\text{Pcy}_2](\text{Cl})\text{C}_6\text{H}_6$ [26] (at 183 K), and monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_7\text{H}_8\text{N})\text{PPh}_2\}(\text{Cl})]$ [27] in which Cl^- anions complete inner coordinate spheres ($\text{PtP}^1\text{N}^1\text{P}^2\text{Cl}$).

In the remaining two complexes, triclinic $[\text{Pt}\{\eta^3\text{-(}\eta^2\text{-(C}_{24}\text{H}_{44})\text{P}(\text{C}_7\text{H}_6\text{N})\text{P}(\text{C}_{24}\text{H}_{44})\}(\text{PPh}_3)]\cdot 2\text{CH}_2\text{Cl}_2$ [28] (at 103 K) and monoclinic $[\text{Pt}\{\eta^3\text{-(}\eta^2\text{-C}_{18}\text{H}_{28})\text{P}(\text{C}_7\text{H}_6\text{N})\text{P}(\eta^2\text{-C}_{18}\text{H}_{29})\}(\text{P}^3\text{cy}_3)]$ [29] (at 103 K), a monodentate P^3L is involved ($\text{PtP}^1\text{N}^1\text{P}^2\text{P}^3$).

The total mean Pt-L bond distance elongates in the following sequences:

$\text{Pt}(\eta^3\text{-P}^1\text{N}^1\text{P}^2)(\text{Y})$, $\text{Y} = \text{N}^2\text{L}$, CL , Cl , P^3L (19 examples): Pt-N^1 : (trans to Y): 2.024 (3) Å (N^2) < 2.077 (2,5) Å (P^3) < 2.128 (2,70) Å (C) < 2.201 (3,26) Å (Cl); Pt-Y : (trans to N^1): 2.056 (3) Å (N^2) < 2.072 (2,85) Å (C) < 2.277 (2,5) Å (P^3) < 2.316 (2,17) Å (Cl); $\text{Pt-P}^{1,2}$: (mutually trans) is 2.287 (2,17) Å

2.3. $\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y})$, ($\text{Y} = \text{OL} (x4)$, $\text{NL}(x4)$, $\text{C}^2\text{L} (x9)$, $\text{Cl} (x12)$, $\text{Br} (x2)$)

There are over thirty examples of the $\text{P}^1\text{C}^1\text{C}^2\text{P}^2$ metallocycle type, and their structural data are summarized in Table 2. The chemical structures and practical applications of these particular complexes are presented in Table S2. In four complexes, monoclinic $[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2\}(\text{H}_2\text{O})]\cdot\text{SbF}_6$ [30], triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{Ph}_2\text{P}\}(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3$ [31], triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2\}(\text{OMe})]\cdot 0.5\text{C}_6\text{H}_6$ [31], and orthorhombic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_{20}\text{H}_{11})\text{PPri}^i_2\}(\text{OOC}\text{CF}_3)]$ [32] (Figure 2), a monodentate OL ligand completed a square planar geometry ($\text{PtP}^1\text{C}^1\text{P}^2\text{O}$).

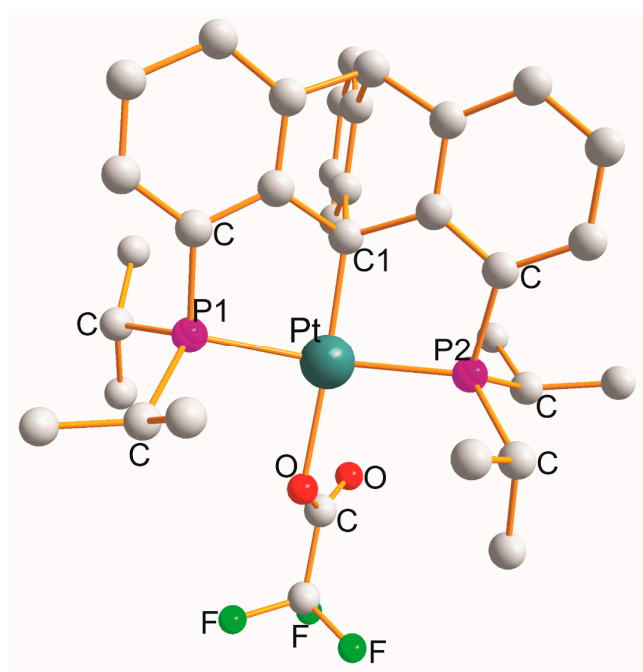


Figure 2. Structure of $[\text{Pt}\{\eta^3\text{-Pri}_2\text{P}(\text{C}_{20}\text{H}_{11})\text{PPri}^i_2\}(\text{OOC}\text{CF}_3)]$ [32].

In four complexes, monoclinic $[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2\}(\text{NC}_5\text{H}_5)]\text{B}(\text{C}_6\text{H}_5)_4$ [30], orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{20}\text{H}_{13}\text{O}_4)\text{PPh}_2\}(\text{N}\equiv\text{CCH}_3)]\text{BF}_4$ [32], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{20}\text{H}_{11}\text{O}_2)\text{PPh}_2\}(\text{NC}_5\text{H}_5)]\text{Cl}] (\text{NC}_5\text{H}_5)$ [33], and monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{20}\text{H}_{11}\text{O}_4)\text{PPh}_2\}(\text{N}\equiv\text{CCH}_3)]\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$ [33], monodentate NL ligands completed the inner coordination sphere $\text{PtP}^1\text{N}^1\text{P}^2\text{N}^2$.

There are nine complexes, tetragonal $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{24}\text{H}_{19}\text{O}_2)\text{PPh}_2\}(\text{CN})]$ [34], triclinic $[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2\}(\text{CO})]\text{SbF}_6$ [35], monoclinic $[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2\}(\text{CH}_3)]$ [35], monoclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_8\text{H}_7)\text{PPri}^i_2\}(\text{CO})]\text{CF}_3\text{SO}_3\cdot 0.5\text{C}_6\text{H}_6$ [36], monoclinic $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_8\text{H}_7)\text{PBu}^t_2\}(\eta^1\text{-CHOMe})]\text{CF}_3\text{SO}_3\cdot\text{thf}$ [36], orthorhombic $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_{12}\text{H}_9)\text{PBu}^t_2\}(\text{CO})]\text{BF}_4$ [37], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2\}(\eta^1\text{-C}_{12}\text{H}_{19}\text{N}_2)]$ [38], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_7\text{N}_2)\text{PPh}_2\}(\eta^1\text{-C}_3\text{F}_2)]$ [39], and monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2\}(\eta^1\text{-C}_{12}\text{H}_{21}\text{N}_2)]\cdot 2(\text{BF}_4)$ [40], in which a monodentate C^2L ligands are involved ($\text{PtP}^1\text{C}^1\text{P}^2\text{C}^2$).

In twelve complexes, triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{20}\text{H}_{11}\text{O}_2)\text{PPh}_2\}(\text{Cl})](\text{CH}_3\text{CN})_4$ [33], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{24}\text{H}_{19}\text{O}_2)\text{PPh}_2\}(\text{Cl})]$ [34], monoclinic $[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2\}(\text{Cl})]1.5\text{C}_6\text{H}_{14}$ [35], orthorhombic $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{Bu}^t_2)\}(\text{Cl})]$ [36], monoclinic $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_{12}\text{H}_9)\text{P}(\text{Bu}^t_2)\}(\text{Cl})]$ [37], monoclinic $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{Bu}^t_2)\}(\text{Cl})]$ [41], triclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{Pr}^i_2)\}(\text{Cl})]$ [42], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{14}\text{H}_7)\text{PPh}_2\}(\text{Cl})]$ [43], monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2\}(\text{Cl})]\text{CH}_3\text{CN}$ [44], orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{18}\text{H}_{11}\text{O}_8)\text{PPh}_2\}(\text{Cl})]\text{CH}_3\text{CN}$ [44], orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{18}\text{H}_{11}\text{O}_8)\text{PPh}_2\}(\text{Cl})]\text{CH}_2\text{C}_{12}$ [45], and monoclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_{20}\text{H}_{11})\text{P}(\text{Pr}^i_2)\}(\text{Cl})](\text{CH}_3\text{CN})_2$ [46], a Cl^- anion completed inner coordination spheres around each Pt(II) atom ($\text{PtP}^1\text{C}^1\text{P}^2\text{Cl}$).

A Br^- anion is involved in two monoclinic complexes, $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2\}(\text{Br})]$ [57] and $[\text{Pt}\{\eta^3\text{-Bu}^t_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{Bu}^t_2)\}(\text{Br})]$ [47].

The total mean PL-L bond distance elongates in the following sequences:

$\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y})$, $\text{Y} = \text{OL}, \text{NL}, \text{C}^2\text{L}, \text{Cl}, \text{Br}$ (31 examples): $\text{Pt}-\text{Cl}$: (*trans* to Y): 2.001 (3,8) Å (N) < 2.027 (2,8) Å (O) ~ 2.027 (2,6) Å (Br) < 2.031 (2,12) Å (Cl) < 2.049 (2) Å (C²); $\text{Pt}-\text{Y}$: (*trans* to C¹): 2.065 (7,12) Å (C²) < 2.085 (2,12) Å (N) < 2.132 (2,9) Å (O) < 2.400 (2,16) Å (Cl) < 2.467 (1,10) Å (Br); $\text{Pt}-\text{P}^{1,2}$: (mutually *trans*) is 2.75 (2,12) Å.

2.4. $\text{Pt}(\eta^3\text{-P}^1\text{S}^1\text{P}^2)(\text{Y})$, ($\text{Y} = \text{CH}_3$ (x1), Cl (x2), P^3Ph_3 (x2), I (x1))

There are six complexes in which each heterotridentate ligand creates a $\text{P}^1\text{C}_2\text{S}^1\text{C}_2\text{P}^2$ metallocycle. Monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(\text{=O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{CH}_3)]\text{PF}_6\cdot\text{CH}_3\text{CN}$ [48] (at 100 K; Figure 3) is the only example with a ($\text{PtP}^1\text{S}^1\text{P}^2\text{C}$) chromophore. In monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(\text{=O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{Cl})]\text{PF}_6\cdot\text{CH}_3\text{CN}$ [48] and triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{=O})(\text{CH}_2)_2\text{PPh}_2\}(\text{Cl})]\text{ClO}_4$ [49], the Cl^- anion completed a square planar geometry ($\text{PtP}^1\text{S}^1\text{P}^2\text{Cl}$). The structural data are summarized in Table 3. The chemical structures and practical applications of these particular complexes are presented in Table S3.

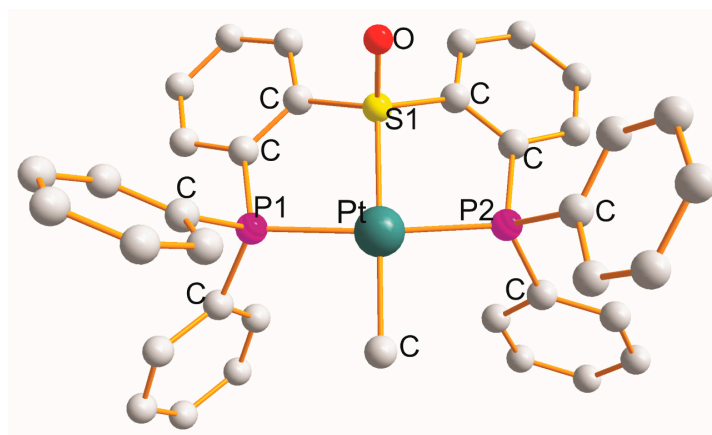


Figure 3. Structure of $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(\text{=O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{CH}_3)]$ [49].

In triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(\text{=O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{P}^3\text{Ph}_3)]0.5\cdot\text{CH}_2\text{Cl}$ [48] (at 100 K) and orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2\}(\text{P}^3\text{Ph}_3)]\text{ClO}_4$ [50] (at 100 K), the P^3Ph_3 are involved ($\text{PtP}^1\text{S}^1\text{P}^2\text{P}^3$).

In another triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{23}\text{H}_{28}\text{S})\text{PPh}_2\}(\text{I})]1.74\text{CH}_2\text{Cl}_2$ [51] (at 150 K), the I^- anion is involved ($\text{PtP}^1\text{S}^1\text{P}^2\text{I}$).

The total mean PL-L bond distance elongates in the sequences:

$\text{Pt}(\eta^3\text{-P}^1\text{S}^1\text{P}^2)(\text{Y})$, $\text{Y} = \text{CL}, \text{Cl}, \text{P}^3\text{L}, \text{I}$ (6 examples): $\text{Pt}-\text{S}^1$: (*trans* to Y): 2.187 (2,5) Å (Cl) < 2.256 (2) Å (I) < 2.268 (2) Å (C) < 2.328 (2,15) Å (P³); $\text{Pt}-\text{Y}$: (*trans* to S¹): 2.093 (2) Å (C) < 2.285 (2,3) Å (P³) < 2.317 (2,5) Å (Cl) < 2.510 (1) Å (I); $\text{Pt}-\text{P}^{1,2}$: (mutually *trans*) is 2.300 (4,30) Å.

2.5. $\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Y})$, ($\text{Y} = \text{H}$ (x2), OL (x1), NL (x1), CL (x1), Cl (x5), P^3L (x1))

There are fourteen complexes in which each heterotridentate ligand creates a pair of “equal” five-membered metallocyclic rings with a common Si¹ atom of the $\text{P}^1\text{C}_2\text{Si}^1\text{C}_2\text{P}^2$

type. The structural data are summarized in Table 3. The chemical structures and practical applications of these particular complexes are presented in Table S3. In two monoclinic $[\text{Pt}\{\eta^3\text{-cy}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{Pcy}_2\}(\text{H})].0.5 \text{ pentane}$ [52] (at 150 K) and $[\text{Pt}\{\eta^3\text{-cy}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{Pcy}_2\}(\text{H})].1.25 \text{ pentane}$ [52] (at 93 K), hydride completed a square planar geometry ($\text{PtP}^1\text{Si}^1\text{P}^2\text{H}$).

Triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{OEt}_2)]\{\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{Ph})\}.\text{OEt}_2$ [53] (Figure 4) is the only example with a monodentate OEt_2 ligand ($\text{PtP}^1\text{Si}^1\text{P}^2\text{O}$).

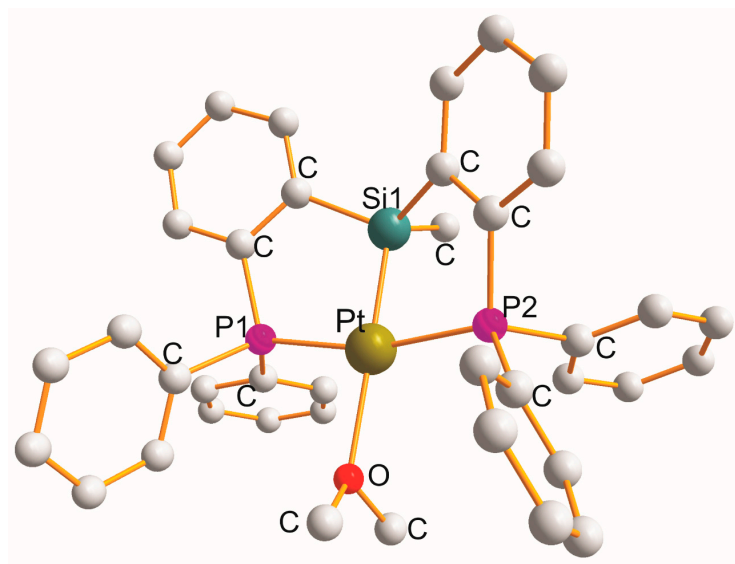


Figure 4. Structure of $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{OEt}_2)]$ [53].

In another triclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}^1(\text{C}_6\text{H}_4)\text{Si}^1(\text{C}_6\text{H}_4)\text{P}^2\text{Pr}^i_2\}(\text{NC}_5\text{H}_5)]\text{B}(\text{C}_8\text{H}_3\text{F}_6)_4$ [58] (at 100 K), a monodentate NC_5H_5 is involved ($\text{PtP}^1\text{Si}^1\text{P}^2\text{N}$).

In the following four complexes: triclinic $[\text{Pt}\{\eta^3\text{-cy}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{Pcy}_2\}(\text{Ph})]\text{OEt}_2$ [53] (at 173 K), triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{CH}_2\text{Ph})]\text{CH}_2\text{Cl}_2$ [53] (at 193 K), triclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{OH})(\text{C}_6\text{H}_4)\text{P}^2\text{Pr}^i_2\}(\text{CO})]\text{B}(\text{C}_6\text{F}_5)_4$ [54] (at 120 K), and orthorhombic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{H})(\text{C}_6\text{H}_4)\text{P}^2\text{Pr}^i_2\}(\text{mes})]$ [55] (at 110 K), monodentate CL ligands are involved ($\text{PtP}^1\text{Si}^1\text{P}^2\text{C}$).

In the following five complexes: monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{Cl})]$ [53] (at 173 K), orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{ClAlCl}_3)](\text{C}_6\text{H}_5\text{F})_2$ [53] (at 193 K), monoclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{OH})(\text{C}_6\text{H}_4)\text{P}^2\text{Pr}^i_2\}(\text{Cl})]$ [54] (at 120 K), monoclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{H})(\text{C}_6\text{H}_4)\text{Pcy}_2\}(\text{Cl})]$ [55] (at 110 K), and monoclinic $[\text{Pt}\{\eta^3\text{-cy}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{Pcy}_2\}(\text{Cl})]$ [56] (at 110 K), tridentate $\text{P}^1\text{Si}^1\text{P}^2$ with Cl^- anions construct inner coordination spheres around each Pt(II) atom ($\text{PtP}^1\text{Si}^1\text{P}^2\text{Cl}$).

The total mean PL-L bond distance elongates in the following sequences:

$\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Y})$, $\text{Y} = \text{H}, \text{OL}, \text{NL}, \text{CL}, \text{Cl}, \text{P}^3\text{L}$ (19 examples): Pt-Si^1 : (*trans* to Y): $2.276(2) \text{ \AA} (\text{O}) < 2.279(2,6) \text{ \AA} (\text{Cl}) < 2.315(2) \text{ \AA} (\text{N}) < 2.331(2,5) \text{ \AA} (\text{H}) < 2.339(2,17) \text{ \AA} (\text{C}) < 2.369(2) \text{ \AA} (\text{P}^3)$; Pt-Y : $1.51(1,2) \text{ \AA} (\text{H}) < 2.122(2,6) \text{ \AA} (\text{C}) < 2.222(2) \text{ \AA} (\text{N}) < 2.282(2) \text{ \AA} (\text{O}) < 2.316(2) \text{ \AA} (\text{P}^3) < 2.451(2,13) \text{ \AA} (\text{Cl})$; $\text{Pt-P}^{1,2}$: (mutually *trans*) is $2.289(2,32) \text{ \AA}$.

The structure of monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}^1(\text{C}_6\text{H}_4)\text{Si}^1(\text{Me})(\text{C}_6\text{H}_4)\text{P}^2\text{Ph}_2\}(\text{P}^3\text{Ph}_3)]$ [59] (at 123 K) is shown in Figure 5. In a distorted trigonal-pyramidal geometry, three P atoms construct a trigonal plane, and the Si^1 atom occupies a pyramid. The heterotridentate $\text{P}^1\text{Si}^1\text{P}^2$ ligand forms a pair of “equal” five-membered metallocyclic rings with a common Si^1 atom of the $\text{P}^1\text{C}_2\text{Si}^1\text{C}_2\text{P}^2$ type, with the mean $\text{P}^1\text{-Pt-Si}^1/\text{Si}^1\text{-Pt-P}^2$ bite angles of $83.3(1,8)^\circ$. The values for the remaining angles are $120.7(2)^\circ$ ($\text{P}^1\text{-Pt-P}^2$), $119.6(2,2,4)^\circ$ ($\text{P}^1\text{-Pt-P}^3/\text{P}^3\text{-Pt-P}^2$), and $108.9(2)^\circ$ ($\text{Si}^1\text{-Pt-P}^3$). The Pt-L bond distance elongates in the following order: $2.290(2,11) \text{ \AA} (\text{Pt-P}^1, \text{Pt-P}^2) < 2.318(2) \text{ \AA} (\text{Pt-P}^3) < 2.369(2) \text{ \AA} (\text{Pt-Si}^1)$. This is the only example of such geometries.

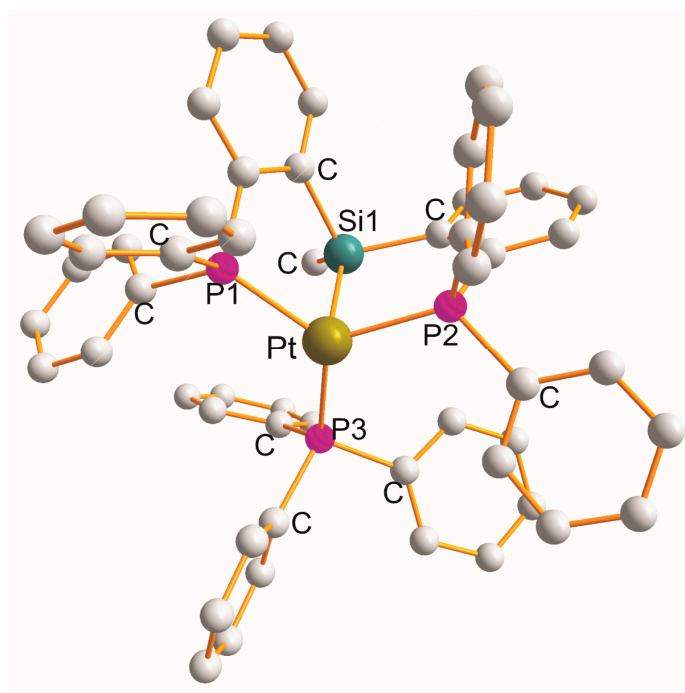


Figure 5. Structure of $[\text{Pt}(\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2)(\text{PPh}_3)]$ [59].

3. Conclusions

This review evaluates seventy Pt(II) complexes in which inner coordination spheres are constructed by heterotridentate organodiphosphines ($\eta^3\text{-P}^1\text{X}^1\text{P}^2$) (Y), ($\text{X}^1 = \text{OL}, \text{NL}, \text{CL}, \text{SL}$ or SiL) with variable monodentate donor ligands. These complexes crystallized in five crystal systems: trigonal ($\times 1$), tetragonal ($\times 1$), orthorhombic ($\times 11$), triclinic ($\times 18$), and monoclinic ($\times 39$).

The structures of the complexes are similar. Each heterotridentate organodiphosphine ligand creates a pair of “equal” five-membered metallocyclic rings with a common X^1 atom of the $\text{P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2$ type.

The sum of four ($\text{Pt-P}(\times 2) + \text{Pt-X}^1 + \text{Pt-Y}$) bond distances grows with the covalent radius of the Y atom in the following sequences:

$\text{PtP}^1\text{N}^1\text{P}^2\text{Y}$: $8.65 \text{ \AA}$ ($\text{Y} = \text{N}$) $< 8.76 \text{ \AA}$ (C) $< 8.91 \text{ \AA}$ (Cl) $< 9.00 \text{ \AA}$ (P^3);

$\text{PtP}^1\text{C}^1\text{P}^2\text{Y}$: $8.64 \text{ \AA}$ ($\text{Y} = \text{N}$) $< 8.66 \text{ \AA}$ (C^2) $< 8.98 \text{ \AA}$ (Cl) $< 9.05 \text{ \AA}$ (Br);

$\text{PtP}^1\text{S}^1\text{P}^2\text{Y}$: $8.91 \text{ \AA}$ ($\text{Y} = \text{C}$) $< 9.13 \text{ \AA}$ (Cl) $< 9.20 \text{ \AA}$ (P^3) $< 9.39 \text{ \AA}$ (I);

$\text{PtP}^1\text{Si}^1\text{P}^2\text{Y}$: $8.35 \text{ \AA}$ ($\text{Y} = \text{H}$) $< 9.15 \text{ \AA}$ (O) $< 9.17 \text{ \AA}$ (N) $< 9.30 \text{ \AA}$ (Cl).

The total mean values of the L-Pt-L bond angles are $83.1 (2.2.7)^\circ$ ($\text{P}^1\text{-Pt-X}^1/\text{X}^1\text{-Pt-P}^2$), $163.2 (2.3.5)^\circ$ ($\text{P}^1\text{-Pt-P}^2$), $96.2 (2.2.5)^\circ$ ($\text{P}^1\text{-Pt-Y}/\text{Y-Pt-P}^2$), and $175.7^\circ (2.3.9)$ ($\text{X}^1\text{-Pt-Y}$).

There are two exceptions— $\text{PtP}^1\text{C}^1\text{P}^2\text{O}$ and $\text{PtP}^1\text{Si}^1\text{P}^2\text{C}$ —with the sums of 8.71 and 9.03 Å that do not follow the covalent radius of the Y atom. There are two reasons for this discrepancy: *trans*-influence of C^1 vs. O and Si^1 vs. C, and the types of ligand H_2O and OMe in the former and CO and CN in the latter.

It is well known that in four-coordinated Pt(II) atoms, there is a preference for square planar geometry with different degrees of distortion. A simple metric to assess the molecular shape and degree of distortion is the parameter T_4 for square planar geometry according to the following equation: $T_4 = 360 - (\alpha + \beta)/141$ [60]. The value of T_4 for a perfect square planar geometry is zero. The degree of distortion for a square planar geometry around Pt(II) atoms grows in the following sequences (according to Y):

$\text{Pt}(\eta^3\text{-P}^1\text{S}^1\text{P}^2)(\text{Y})$: $0.105 (\text{Y} = \text{C}^2) < 0.120 (\text{I}) < 0.138 (\text{Cl}) < 0.143 (\text{P}^3)$;

The total mean value of τ_4 is 0.125;

$\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y})$: $0.130 (\text{Cl}) < 0.133 (\text{C}^2) < 0.138 (\text{Br}) < 0.146 (\text{O}^2) < 0.166 (\text{N}^2)$;

The total mean value of τ_4 is 0.143;

$\text{Pt}(\eta^3\text{-P}^1\text{N}^1\text{P}^2)(\text{Y})$: $0.115 (\text{Cl}) < 0.125 (\text{N}^2) < 0.140 (\text{C}^2) < 0.204 (\text{P}^3)$;

The total mean value of τ_4 is 0.146;

$\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y}):0.163 (\text{P}^3)$;

$\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Y}):0.115(\text{O}^2) < 0.169(\text{H}) < 0.171 (\text{N}^2) < 0.176 (\text{Cl}) < 0.186 (\text{C}^2)$;

The total mean value of τ_4 is 0.163.

The $\text{trans-}\alpha\text{-X}^1\text{-Pt-Y}$ and $\beta\text{-P}^1\text{-Pt-P}^2$ bond angles are responsible for distortion of square planar geometry around Pt(II) atoms. While the donor atoms of $\alpha\text{-X}^1\text{-Pt-Y}$ angles exhibit a wide variety of soft (H, C, S, P, Si, I), borderline (Br), and hard (O, N, Cl), the donor atoms of $\beta\text{-P}^1\text{-Pt-P}^2$ angles are only soft. The soft atom ligand has a larger *trans*-effect than the borderline or hard ones. The *trans*-effect on a Pt bond distance also affects the L-Pt-L bond angles.

If we take *trans*-effect into account, the respective *trans-}\alpha\text{-X}^1\text{-Pt-Y} and $\beta\text{-P}^1\text{-Pt-P}^2$ angles open, and the distortion (τ_4) diminishes in the order (means values) (Table 4).*

Table 4. Total mean values of angles and τ_4 of the respective complexes according to the plasticity of atoms.

Donor Atoms	$\alpha\text{-X}^1\text{-Pt-Y}$ (°)	$\beta\text{-P}^1\text{-Pt-P}^2$ (°)	τ_4
$\text{X}^1(\text{S})\text{-Pt}(\text{H})\text{Y}$	162.2	175.6	0.151
$\text{X}^1(\text{S})\text{-Pt}(\text{B})\text{Y}$	164.9	175.5	0.138
$\text{X}^1(\text{S})\text{-Pt}(\text{S})\text{Y}$	164.3	175.5	0.128
$\text{X}^1(\text{H})\text{-Pt}(\text{H})\text{Y}$	166.8	176.2	0.054

S—soft; H—hard; B—borderline; P^1 , P^2 —soft.

Structural information about platinum complexes is a prerequisite to properly understanding their roles in chemistry, biology, medicine, etc. Hence, this structural study provides relevant and rationally classified data on the evaluated group of Pt(II) complexes ($\text{Pt}(\eta^3\text{-P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2)(\text{Y}))$, which is helpful for the proper interpretation of results from the areas where such complexes were applied (here, mainly toward their catalytic activity).

Supplementary Materials: The following are available at <https://www.mdpi.com/article/10.3390/cryst13091340/s1>, Table S1: Structures and applications of $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{O}^1, \text{N}^1$), ($\text{Y} = \text{C}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{P}^3\text{L}$) complexes; Table S2: Structures and applications of $\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y})$, ($\text{Y} = \text{O}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{Cl}, \text{Br}$) complexes; Table S3: Structures and applications of $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{S}^1$ or Si^1) ($\text{Y} = \text{C}^2\text{L}, \text{Cl}, \text{P}^3\text{L}, \text{I}, \text{H}, \text{O}^2\text{L}$) complexes.

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Abbreviations

$\text{Bu}^t_2\text{P}(\text{C}_{11}\text{H}_{16}\text{N}_3)\text{PBu}^t_2$	(<i>N,N'</i> -3,3,5 triethylpyridine-2,6-(1 <i>H</i> ,2 <i>H</i>)-diylidene)bis(di- <i>t</i> -butyl(phosphin)usamidato)
$\text{Bu}^t_2\text{P}(\text{C}_{12}\text{H}_9)\text{PBu}^t_2$	(1,3-bis(di- <i>t</i> -butylphosphinomethyl)-2-naphthyl
$\text{Bu}^t_2\text{P}(\text{C}_7\text{H}_6\text{N})\text{PBu}^t_2$	(6-((di- <i>t</i> -butylphosphino)methyl-2-((di- <i>t</i> -butylphosphino)methylene)-1,2-dihydropyridine-1-yl)
$\text{Bu}^t_2\text{P}(\text{C}_7\text{H}_7\text{N})\text{PBu}^t_2$	(2,6-bis(di- <i>t</i> -butylphosphino)methyl)pyridine
$(\text{CF}_3)_2\text{P}(\text{C}_8\text{H}_7)\text{P}(\text{CF}_3)_2$	(2,6-bis(bis(trifluoromethyl)phosphinomethyl) phenyl)

$(\eta^2\text{-C}_{18}\text{H}_{28})\text{P}(\text{C}_7\text{H}_6\text{N})\text{P}(\eta^1\text{-C}_{18}\text{H}_{24})$	(2-((5,7-di- <i>t</i> -butyl-3,3-dimethyl-2,3-dihydro-14-phosphindol-1-yl)methylene)-6-(((2,4,6-tri- <i>t</i> -butylphenylphosphino)methyl)-1,2-dihydro pyridinyl) undecachloro-carba-undecaborane
$\text{Cy}_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{Me})(\text{C}_6\text{H}_4)\text{PCy}_2$	((methylsilanediyl)di-2,1-phenylene)bis(dicyclohexylphosphine))
Pcy_3	tricyclohexylphosphino
$\text{Ph}_2\text{P}(\text{C}_{12}\text{H}_8\text{N})\text{PPh}_2$	(2,2'-bis (diphenylphosphino)diphenylamido)
$\text{Ph}_2\text{P}(\text{C}_{14}\text{H}_7)\text{PPh}_2$	(1,8-bis(diphenylphosphino)-9-anthryl)
$\text{Ph}_2\text{P}(\text{C}_{14}\text{H}_7\text{O}_2)\text{PPh}_2$	(1,8-bis(diphenylphosphino)-9-hydroxy-10-oxo-9,10-dihydroanthracen-9-yl)
$\text{Ph}_2\text{P}(\text{C}_{15}\text{H}_{12}\text{O})\text{PPh}_2$	((9,9-dimethyl-9 <i>H</i> -xanthene-4,5-diyl)bis (diphenylphosphine)-diphenyl(2-pyridyl) phosphine
$\text{Ph}_2\text{P}(\text{C}_{18}\text{H}_{19}\text{O}_8)\text{PPh}_2$	(2,6-bis(1-(diphenylphosphino)-3-methoxy-2-(methoxycarbonyl)-3-oxopropylphenyl)
$\text{Ph}_2\text{P}(\text{C}_{20}\text{H}_{11}\text{O}_2)\text{PPh}_2$	(13,16-bis(diphenylphosphino)-3,6-dihydroxypentacyclo [6.6.6.0 ^{2,7} .0 ^{9,14} .0 ^{15,20}]icosa-2,4,6,9,11,13,15,17,19-nonaen-1-yl)
$\text{Ph}_2\text{P}(\text{C}_{20}\text{H}_{13}\text{O}_4)\text{PPh}_2$	(3,13-bis(diphenylphosphino)-15,16-bis(methoxy-carbonyl)tetracyclo [6.6.6.2.0 ^{2,7} .0 ^{9,14}]hexadeca-2,4,6,9,11,13,15-heptaen-1-yl)
$\text{Ph}_2\text{P}(\text{C}_{23}\text{H}_{28}\text{S})\text{PPh}_2$	((9,9-dimethyl-2,7-bis(<i>t</i> -butyl)-9 <i>H</i> -thioxantene-4,5-diyl)bis(diphenylphosphine)
$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(=\text{O})(\text{C}_6\text{H}_4)\text{PPh}_2$	((sulfinyldi-2,1-phenylene)bis(diphenylphosphine)
$\text{Ph}_2\text{P}(\text{C}_8\text{H}_7)\text{PPh}_2$	(2,6-bis((diphenylphosphino)methyl)phenyl)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2$	(bis(2-(diphenylphosphino)ethyl)sulfide)
PPh_3	triphenylphosphine
$\text{Pr}^i_2\text{P}(\text{C}_{20}\text{H}_{11})\text{PPr}^i_2$	(3,13-bis(diisopropylphosphino)-pentacyclo [6.6.6.0 ^{2,7} .0 ^{9,14} .0 ^{15,20}]icosa-2,4,6,9,11,13,15,17,19-heptaen-1-yl)
$\text{Pr}^i_2\text{P}(\text{C}_{12}\text{H}_6\text{F}_2\text{N})\text{PPr}^i_2$	(2-(diisopropylphosphino)- <i>N</i> -(2-(diisopropyl-phosphino)-4-fluorophenyl)-4-fluoroanilinato)
$\text{Pr}^i_2\text{P}(\text{C}_{12}\text{H}_7\text{F}_2\text{N})\text{PPr}^i_2$	(2-(diisopropylphosphino)- <i>N</i> -(2-(diisopropyl-phosphino)-4-fluorophenyl)-4-fluoroaniline)
$\text{Pr}^i_2\text{P}(\text{C}_{14}\text{H}_{12}\text{N})\text{PPh}_2$	(bis(2-(di-isopropylphosphino)-4-methyl-phenyl)(2-((diphenylphosphino)-4-methyl-phenyl)amide)
$\text{Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{C}_{12}\text{H}_{46}\text{P})(\text{C}_6\text{H}_4)\text{PPr}^i_2$	(tris(2-(diisopropylphosphino)phenyl)silyl)
$\text{Pr}^i_2\text{P}(\text{C}_6\text{H}_4)\text{Si}(\text{H})(\text{C}_6\text{H}_4)\text{PPr}^i_2$	((silanediyl)di-2,1-phenylene)bis(diiso-propyl phosphine))

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