# Heterotridentate Organomonophosphines in $\operatorname{Pt}\left(\kappa^{3}-\mathrm{X}^{1} \mathrm{P}^{1} \mathrm{X}^{2}\right)(\mathrm{Y})$ $\left(X^{1,2}=N^{1,2}\right.$ or $\left.\mathbf{S}^{1,2}\right), \operatorname{Pt}\left(\kappa^{3}-P^{1} \mathbf{N}^{1} \mathbf{X}^{1}\right)(Y)\left(X^{1}=\mathbf{O}, C, S\right.$ or $\left.S e\right)$ $\operatorname{Pt}\left(\kappa^{3}-\mathbf{P}^{1} \mathbf{S}^{1} \mathrm{Cl}^{1}\right)(\mathrm{Cl})$ and $\mathrm{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathbf{N}^{1}\right)(\mathrm{OL})-S t r u c t u r a l$ Aspects 

Milan Melník ${ }^{1,2, *}$ and Peter Mikuš ${ }^{1,3}$ (D)

1 Comenius University Bratislava, Faculty of Pharmacy, Department of Pharmaceutical Analysis and Nuclear Pharmacy, Odbojárov 10, SK-832 32 Bratislava, Slovakia
2 Slovak Technical University, Faculty of Chemical and Food Technology, Radlinskeho 9, SK-812 37 Bratislava, Slovakia
3 Comenius University Bratislava, Faculty of Pharmacy, Toxicological and Antidoping Centre, Odbojárov 10, SK-832 32 Bratislava, Slovakia

* Correspondence: mikus@fpharm.uniba.sk

Citation: Melník, M.; Mikuš, P. Heterotridentate Organomonophosphines in $\operatorname{Pt}\left(\kappa^{3}-X^{1} \mathrm{P}^{1} \mathrm{X}^{2}\right)(\mathrm{Y})\left(\mathrm{X}^{1,2}=\mathrm{N}^{1,2}\right.$ or $\left.\mathrm{S}^{1,2}\right)$, $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{X}^{1}\right)(\mathrm{Y})\left(\mathrm{X}^{1}=\mathrm{O}, \mathrm{C}, \mathrm{S}\right.$ or Se$)$ $\mathrm{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}\right)(\mathrm{Cl})$ and $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}\right)(\mathrm{OL})$ —Structural Aspects. Crystals 2022, 12, 1772. https: / /doi.org/10.3390/ cryst12121772

Academic Editor: Andrei Vladimirovich Shevelkov

Received: 21 November 2022
Accepted: 1 December 2022
Published: 6 December 2022
Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

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/).


#### Abstract

This review covers twenty four $\mathrm{Pt}(\mathrm{II})$ complexes of the inner coordination sphere $\mathrm{Pt}\left(\mathrm{\kappa}^{3}-\mathrm{P}^{1}\right.$ $\left.\mathrm{N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y}),(\mathrm{Y}=\mathrm{Cl}, \mathrm{CL}) ; \mathrm{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{X}^{1}\right)(\mathrm{Y}),\left(\mathrm{X}^{1}=\mathrm{O}^{1}\right.$ and $\left.\mathrm{Y}=\mathrm{P}^{2} \mathrm{~L}, \mathrm{Cl}, \mathrm{I}\right) ;\left(\mathrm{X}^{1}=\mathrm{C}^{1}\right.$ and $\left.\mathrm{Y}=\mathrm{NL}, \mathrm{Cl}\right)$; $\left(\mathrm{X}^{1}=\mathrm{S}^{1}\right.$ and $\left.\mathrm{Y}=\mathrm{Cl}, \mathrm{I}\right) ;\left(\mathrm{X}^{1}=\mathrm{Se}^{1}\right.$ and $\left.\mathrm{Y}=\mathrm{Cl}\right) ; \mathrm{Pt}\left(\mathrm{K}^{3}-\mathrm{N}^{1} \mathrm{P}^{1} \mathrm{~N}^{2}\right)(\mathrm{Cl}), \mathrm{Pt}\left(\mathrm{K}^{3}-\mathrm{S}^{1} \mathrm{P}^{1} \mathrm{~S}^{2}\right)(\mathrm{Cl}), \mathrm{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl} \mathrm{l}^{1}\right)(\mathrm{Cl})$ and $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}\right)(\mathrm{OL})$. These complexes are crystallized in three crystal classes: monoclinic ( 16 examples), triclinic ( 5 examples), and orthorhombic ( 3 examples). Each $\mathrm{k}^{3}$-ligand creates two metallocyclic rings with various combinations of the respective metallocyclic rings. If the common central ligating atom is $\mathrm{N}^{1}$, the $5+5$ membered, $5+5,5+6,6+5$, and $6+6$; if the common central ligating atom is $\mathrm{P}^{1}: 5+5$, and $6+6$; if the common central ligating atom is $\mathrm{S}^{1}$ or $\mathrm{Si}^{1}, 5+6$-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 $\mathrm{Pt}(\mathrm{II})$ atoms as well as trans-influence. The sums of the $\mathrm{Pt}-\mathrm{L}$ $(x=4)$ 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 $\mathrm{Pt}(\mathrm{II})$ atom. There is a relation between the degree of distortion ( $\mathrm{T}_{4}$ ) 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; $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{X}^{1} \mathrm{X}^{2}\right)(\mathrm{Y}) ; \operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{X}^{1} \mathrm{P}^{1} \mathrm{X}^{2}\right)(\mathrm{Y})$; distortion; trans-influence

## 1. Introduction

Platinum exists in a wide range of oxidation states from zero to +6 , including nonintegral, $\mathrm{Pt}(2.25), \mathrm{Pt}(2.81), \mathrm{Pt}(3.25)$ and $\mathrm{Pt}(3.5)$. 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 $\mathrm{Pt}(\mathrm{II})$, the distortion isomers atom is far more common.

Recently, we detail analysed the structural data of distortion isomers of the cis- $\mathrm{Pt}(\mathrm{II})$ 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 $\mathrm{Pt}(\mathrm{II})$ 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:
homodentate ( $\mathrm{P}, \mathrm{PP}, \mathrm{PPP}, \mathrm{PPPP}$ ), heterobi- ( $\mathrm{PO}, \mathrm{PN}, \mathrm{PB}, \mathrm{PS}$ ) and heterotridentate (POP, PNP, PCP, PBP, PSP, PSiP) as well as tetradentate ( $\mathrm{P}_{4}, \mathrm{P}_{3} \mathrm{Si}, \mathrm{P}_{2} \mathrm{~N}_{2}, \mathrm{P}_{2} \mathrm{~S}_{2}, \mathrm{P}_{2} \mathrm{C}_{2}, \mathrm{PN}_{3}$ ) [7-9].

The aim of this survey is to correlate the structural parameters available for heterotridentate organomonophosphines of the types: $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{X}^{1}\right)(\mathrm{Y})\left(\mathrm{X}=\mathrm{N}^{2}, \mathrm{O}^{1}, \mathrm{C}^{1}, \mathrm{~S}^{1}, \mathrm{Se}^{1}\right)$, $\operatorname{Pt}\left(\kappa^{3}-\mathrm{N}^{1} \mathrm{P}^{1} \mathrm{~N}^{2}\right)(\mathrm{Cl}), \mathrm{Pt}\left(\kappa^{3}-\mathrm{S}^{1} \mathrm{P}^{1} \mathrm{~S}^{2}\right)(\mathrm{Cl}), \mathrm{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}\right)(\mathrm{Y})$ and $\mathrm{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}\right)(\mathrm{OL})$.

## 2. Results and Discussion

## 2.1. $\operatorname{Pt}\left(\kappa^{3}-P^{1} N^{1} N^{2}\right)(Y)$ Derivatives

There are nine examples of the $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y})$ type, and their structural parameters are gathered in Table $1\left(\mathrm{~A}: \operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y})\right.$ ). In triclinic $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Bu}^{\mathrm{t}}{ }_{2} \mathrm{P}^{1}\left(\mathrm{CH}_{2}\right)\left(\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}^{1}\right)\right.\right.$ $\left.\left.\left(\mathrm{CH}_{2}\right) \mathrm{N}^{2} \mathrm{Et}_{2}\right\}(\mathrm{Cl})\right] \cdot \mathrm{C}_{6} \mathrm{H}_{6}$ (at 120 K ) [10], heterotridentate $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}$ ligand creates two fivemembered metallocyclic rings with the central common ligating $\mathrm{N}^{1}$ atom of $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2}$ type with the values of the respective rings of $85.5^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $83.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The $\mathrm{Cl}^{-}$completed a square-planar geometry about $\mathrm{Pt}(\mathrm{II})$ atom. The remaining L-Pt-L bond angles open in the sequence $92.6^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<98.5^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<168.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)<$ $176.0^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$. The Pt-L bond distance elongates in the order: $1.997 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$ trans to $\mathrm{Cl})<2.149 \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right.$ trans to $\left.\mathrm{P}^{1}\right)<2.236 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.296 \AA(\mathrm{Pt}-\mathrm{Cl})$.

Table 1. Structural data for $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y})$ and $\operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{X}^{1}\right)(\mathrm{Y})\left(\mathrm{X}^{1}=\mathrm{O}^{1}, \mathrm{C}^{1}, \mathrm{~S}^{1}\right.$ or $\left.\mathrm{Se}^{1}\right)$, $(\mathrm{Y}=\text { variable monodentate atoms/ligands })^{\mathrm{a}}$.

| Complex | Space gr. Cryst. cl. Z | $\begin{aligned} & \mathrm{a}[\mathrm{~A}] \\ & \mathrm{b}[\AA \mathrm{~A}] \\ & \mathrm{c}[\AA \mathrm{~A}] \end{aligned}$ | $\begin{aligned} & \alpha\left[{ }^{\circ}{ }^{\mathbf{\beta}}{ }^{\circ}{ }^{\circ}{ }^{1}\right. \end{aligned}$ | Chromophore (Chelate Rings) $\mathrm{T}_{4}{ }^{\mathrm{b}}$ | $\begin{gathered} \text { Pt-L }{ }^{\text {c }}{ }^{\text {A }} \end{gathered}$ | $\underset{\substack{\text { L-Pt-L }]}}{\left[^{\mathrm{c}}\right.}$ | $\begin{gathered} \text { Ref. } \\ \text { REFCODE } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| A: $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y})$ |  |  |  |  |  |  |  |
|  | $\begin{gathered} \mathrm{tr} \\ \mathrm{Pr}_{1}^{1} \\ 2 \end{gathered}$ | $\begin{aligned} & 9.158(0) \\ & 10.963(0) \\ & 16.018(0) \end{aligned}$ | $\begin{aligned} & 77.29(0) \\ & 76.97(0) \\ & 69.11(0) \end{aligned}$ | $\begin{aligned} & \mathrm{Pttp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{Pl}_{1}^{1}{ }^{1} \mathrm{C}_{2} \mathrm{~N}^{2} \mathrm{C}^{2} \mathrm{~N}^{0.044} \end{aligned}$ | $\mathrm{P}^{1}$ 2.236(1) <br> $\mathrm{N}^{1}$ 1.997(2) <br> $\mathrm{N}^{2}$ 2.149(2) <br> Cl $2.296(2)$ | $\begin{aligned} & \mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{1} 8.5^{\mathrm{d}} \\ & \mathrm{~N}^{1} \mathrm{~N}^{2} 83.4^{\mathrm{d}} \\ & \mathrm{P}^{1} \mathrm{~N}^{2} 186.0 \\ & \mathrm{P}^{1}, \mathrm{Cl} 98.5 \\ & \mathrm{~N}^{2}, \mathrm{Cl} 92.6 \\ & \mathrm{~N}^{1}, \mathrm{Cl} 176.6 \end{aligned}$ | $\begin{gathered} {[10]} \\ \text { WOGDAY } \end{gathered}$ |
| $\begin{gathered} {\left[\mathrm { Ptt } \left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right) .\right.\right.} \\ \left.\left.\left.\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right) \mathrm{N}^{2} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OH}\right)\right)\left(\mathrm{CH}_{3}\right)\right] . \\ (\mathrm{at} 150 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \mathrm{tr}_{\mathrm{Pr}_{1}} \end{gathered}$ | $\begin{aligned} & 9.917(1) \\ & 11.944(2) \\ & 14.872(2) \end{aligned}$ | $\begin{aligned} & 99.17(0) \\ & 103.82(0) \\ & 12.53(0) \end{aligned}$ | $\begin{gathered} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} \\ 0.032 \end{gathered}$ | $\begin{array}{r} \mathrm{P}^{1} 2.179(1) \\ \mathrm{N}^{1} 2.050(2) \\ \mathrm{N}^{2} 2.089(2) \\ \mathrm{H}_{3} \mathrm{C} 2.045(2) \end{array}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 95.3^{\mathrm{e}} \\ \mathrm{~N}^{1} \mathrm{~N}^{2} 80 . \mathrm{m}^{\mathrm{d}} \\ \mathrm{P}^{1} \mathrm{~N}^{2} 173.7 \\ \mathrm{P}^{1}, \mathrm{C} 89.0 \\ \mathrm{~N}^{2}, \mathrm{C} 95.5 \\ \mathrm{~N}^{1}, \mathrm{C} 174.5 \end{gathered}$ | [11] <br> GAJMOV |
| $\begin{gathered} {\left[\mathrm { Pt } \left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right) .\right.\right.} \\ \left.\left.\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right) \mathrm{N}^{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OH}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] . \\ 1.5 \text { toluene } \\ \text { (at } 150 \mathrm{~K}) \end{gathered}$ | $\operatorname{Pa}_{4}{ }_{4}^{\mathrm{m} / \mathrm{c}}$ | $\begin{aligned} & 11.882(1) \\ & 14.184(1) \\ & 21.892(1) \end{aligned}$ | 103.75(0) | $\begin{gathered} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C}^{1} \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{2} \mathrm{C}^{2} \mathrm{~N}^{0.027} \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.184(2) \\ \mathrm{N}^{1} 2.061(3) \\ \mathrm{N}^{2} 2.075(3) \\ \mathrm{H}_{3} \mathrm{C} 2.051(2) \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 95.4^{\mathrm{e}} \\ \mathrm{~N}^{1} \mathrm{~N}^{2} 81.0^{\mathrm{d}} \\ \mathrm{P}^{1}, \mathrm{~N}^{2} 176.4 \\ \mathrm{P}^{1}, \mathrm{C} 90.5 \\ \mathrm{~N}^{2}, \mathrm{C} 93.0 \\ \mathrm{~N}^{1}, \mathrm{C} 174.0 \end{gathered}$ | [11] GAJMUB |
| $\begin{gathered} {\left[\mathrm{Ptt} \mid \mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right) .\right.} \\ \left.\left.\left.\left(\mathrm{C}_{3} \mathrm{H}_{6}\right) \mathrm{N}^{2} \mathrm{C}_{7} \mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] . \\ 2 \text { otouene } \\ (\text { at } 150 \mathrm{~K}) \end{gathered}$ | $\mathrm{P}_{\mathrm{P}_{1} / \mathrm{c}}^{\mathrm{m}}$ | $\begin{aligned} & 14.859(0) \\ & 15.607(0) \\ & 16.287(0) \end{aligned}$ | 95.88(0) | $\begin{gathered} \begin{array}{c} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}^{2} \mathrm{~N}^{2} \\ 0.033 \end{array} \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.189(1) \\ \mathrm{N}^{1} 2.077(2) \\ \mathrm{N}^{2} 2.070(2) \\ \mathrm{H}_{3} \mathrm{C} 2.062(2) \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 95.2^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{~N}^{2} 80 . \mathrm{s}^{\mathrm{d}} \\ \mathrm{P}^{1}, \mathrm{~N}^{2} 175.4 \\ \mathrm{P}^{1}, \mathrm{C} 89.4 \\ \mathrm{~N}^{2}, \mathrm{C} 94.9 \\ \mathrm{~N}^{1}, \mathrm{C} 172.6 \end{gathered}$ | ${ }_{\text {GAJNAI }}^{[11]}$ |
|  | $\underset{\mathrm{P}_{2} / \mathrm{c}}{\mathrm{~m}}$ | $\begin{aligned} & 10.992(0) \\ & 20.133(0) \\ & 16.933(0) \end{aligned}$ | 101.72(0) | $\begin{gathered} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{0} 0.000 \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.184(1) \\ \mathrm{N}^{1} 2.087(2) \\ \mathrm{N}^{2} 2.086(2) \\ \mathrm{H}_{3} \mathrm{C} 2.062(2) \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 92.6^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{~N}^{2} 79.4^{\mathrm{d}} \\ \mathrm{P}^{1}, \mathrm{~N}^{2} 171.8 \\ \mathrm{P}^{1}, \mathrm{C} 91.5 \\ \mathrm{~N}^{2}, \mathrm{C} 96.6 \\ \mathrm{~N}^{1}, \mathrm{C} 173.7 \end{gathered}$ | $\stackrel{[12]}{[12]}_{\text {QICYAD }}$ |
| $\left.\begin{array}{c} {\left[\mathrm{Pt} \mid \mathrm{N}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{5} \mathrm{H}_{7} \mathrm{O}\right)\right.} \\ \left.\mathrm{N}^{2}\left(\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{~N}_{2}\right)\right\}\left(\mathrm{CH}_{3}(\mathrm{at} 93 \mathrm{~K})\right] \mathrm{H}_{3} \\ (\mathrm{at} 9 \mathrm{~K} \end{array}\right)$ | $\underset{\mathrm{P}_{2} / \mathrm{c}}{\mathrm{~m}}$ | $\begin{aligned} & 8.739(1) \\ & 14.98(2) \\ & 25.469(2) \end{aligned}$ | 94.23(0) | $\begin{gathered} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}^{2} \mathrm{~N}^{2} \\ 0.052 \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.190(1) \\ \mathrm{N}^{1} 2.001(2) \\ \mathrm{N}^{2} 2.094(2) \\ \mathrm{H}_{3} \mathrm{C} 2.083(2) \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 89.4^{\mathrm{e}} \\ \mathrm{~N}^{2} \mathrm{~N}^{2} 79.6^{\mathrm{d}} \\ \mathrm{P}^{1} \mathrm{~N}^{2} 169.0 \\ \mathrm{P}^{1}, \mathrm{C} 92.2 \\ \mathrm{~N}^{2}, \mathrm{C} 93.7 \\ \mathrm{~N}^{1}, \mathrm{C} 172.1 \end{gathered}$ | $\begin{gathered} {[13]} \\ \text { DIYYIU } \end{gathered}$ |
| $\begin{gathered} {\left[\mathrm{Pt} \mid \mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right)\right.} \\ \left.\left.\left.\mathrm{N}^{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OH}\right)\left(\mathrm{CH}_{3}\right)\right] \mathrm{Cl}_{2} \mathrm{at} \mathrm{150} \mathrm{~K}\right)\right] \end{gathered}$ | $\underset{\mathrm{P}_{4} / \mathrm{c}}{\mathrm{~m}}$ | $\begin{aligned} & 10.191(0) \\ & 16.86(1) \\ & 17.525(1) \end{aligned}$ | 97.30(0) | $\begin{gathered} \mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} \\ 0.030 \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.183(1) \\ \mathrm{N}^{1} 2.059(1) \\ \mathrm{N}^{2} 2.061(1) \\ \mathrm{H}_{3} \mathrm{C} 2.055(1) \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 95.1^{\mathrm{e}} \\ \mathrm{~N}^{1} \mathrm{~N}^{2} 81 . \mathrm{d}^{\mathrm{d}} \\ \mathrm{P}^{1} \mathrm{~N}^{2} 177.8 \\ \mathrm{P}^{1}, \mathrm{C} 91.2 \\ \mathrm{~N}^{2}, \mathrm{C} 92.6 \\ \mathrm{~N}^{1}, \mathrm{C} 173.4 \end{gathered}$ | CAJLAC |

Table 1. Cont.

| Complex | Space gr. Cryst. cl. Z | $\begin{aligned} & \mathrm{a}[\hat{\AA}] \\ & \mathrm{b}[\hat{A}] \\ & \mathrm{c}[\hat{A}] \end{aligned}$ | $\begin{aligned} & \alpha\left[{ }^{\circ}\right] \\ & \beta\left[{ }^{\circ}\right] \\ & \gamma\left[^{\circ}\right] \end{aligned}$ | Chromophore (Chelate Rings) $\mathrm{T}_{4}{ }^{\mathrm{b}}$ | $\underset{[A \bar{A}]}{\text { Pt-L }}$ | $\mathrm{L}_{\left.\mathrm{L}^{\circ}\right]}$ | $\begin{gathered} \text { Ref. } \\ \text { REFCODE } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \operatorname{tr} \\ { }_{\mathrm{Pi}}^{1} \\ 2 \end{gathered}$ | $\begin{aligned} & 7.431(2) \\ & 10.031(3) \\ & 14.997(5) \end{aligned}$ | $\begin{aligned} & 101.10(0) \\ & 95.70(0) \\ & 98.76(0) \end{aligned}$ | $\begin{gathered} \mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{C} \\ \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{\mathrm{NCCN}} \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1} 2.219(1) \\ & \mathrm{N}^{1} 2.2164(2) \\ & \mathrm{N}^{2} 2.050(1) \\ & \mathrm{Cl} 2.297(2) \end{aligned}$ | $\mathrm{P}^{1} \mathrm{~N}^{1} 95.8^{\mathrm{e}}$ <br> $\mathrm{N}^{1}, \mathrm{~N}^{2} 79.3^{\mathrm{d}}$ <br> $\mathrm{P}^{1}, \mathrm{~N}^{2} 173.0$ <br> P1, Cl 90.8 <br> $\mathrm{N}^{2}, \mathrm{Cl} 94.2$ <br> $\mathrm{N}^{1}$,Cl 173.4 | $\stackrel{\stackrel{[15]}{\text { XUYWEU }}}{ }$ |
| $\begin{gathered} {\left[\mathrm { Pt } \left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{~N}\right)\right.\right.} \\ \left.\left.\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{~N}^{2}\right)\right\}(\mathrm{Cl})\right] \mathrm{PF}_{6} \end{gathered}$ | $\underset{\mathrm{P}_{1} 2_{4} / \mathrm{c}}{\mathrm{~m}^{2}}$ | $\begin{aligned} & 18.910(3) \\ & 10.098(1) \\ & 19.429(3) \end{aligned}$ | 118.93(1) | $\begin{gathered} \mathrm{Ptpl}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2} \mathrm{Cl}_{1}^{1} \mathrm{P}^{1} \mathrm{~N}^{2} \mathrm{CN}^{2} \\ 0.020 \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1} 2.234(1) \\ & \mathrm{N}^{1} 2.120(1) \\ & \mathrm{N}^{2} 2.104(1) \\ & \mathrm{Cl} 2.284(1) \end{aligned}$ | $\mathrm{P}^{1} \mathrm{~N}^{1} 93.3^{\mathrm{e}}$ <br> $\mathrm{N}^{1}, \mathrm{~N}^{2} 85.6^{\mathrm{d}}$ <br> $\mathrm{P}^{1}, \mathrm{~N}^{2} 178.7$ <br> P1, Cl 91.8 <br> $\mathrm{N}^{2}, \mathrm{Cl} 89.2$ <br> $\mathrm{N}^{1}, \mathrm{Cl} 174.0$ | $\begin{aligned} & {[16]} \\ & \text { IFUQEF } \end{aligned}$ |
| B: $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}\right)(\mathrm{Y})$ |  |  |  |  |  |  |  |
|  | $\begin{gathered} \operatorname{tr}_{\mathrm{Pi}}^{1} \\ 2 \end{gathered}$ | $\begin{aligned} & 12.614(2) \\ & 13.671(2) \\ & 15.754(3) \end{aligned}$ | $\begin{gathered} 100.26(0) \\ 99.33(0) \\ 110.68(0) \end{gathered}$ | $\begin{gathered} \mathrm{PtP}^{1 \mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{P}} \\ \mathrm{P}^{\mathrm{C}_{2} \mathrm{~N}^{N} \mathrm{NCO}^{1}} 0.067 \end{gathered}$ | $\begin{array}{ll} \mathrm{P}^{1} & 2.233(2) \\ \mathrm{N}^{1} & 1.985(2) \\ \mathrm{O}^{1} & 2.050(2) \\ \mathrm{LP} & 2.261(1) \end{array}$ | $\begin{gathered} \mathrm{P}^{1} \mathrm{~N}^{1} 83.6^{\mathrm{d}} \\ \mathrm{~N}^{1} \mathrm{O}^{1} 78.8^{\mathrm{d}} \\ \mathrm{P}^{1}, \mathrm{O}^{1} 162.4 \\ \mathrm{P}^{1}, \mathrm{P} 102.9 \\ \mathrm{O}^{1} \mathrm{P} 94.7 \\ \mathrm{~N}^{1}, \mathrm{P} 9173.3 \end{gathered}$ | $\begin{gathered} { }^{[17]} \text { EFODAE } \end{gathered}$ |
| $\begin{gathered} {\left[\mathrm{Ptt} \mathrm{~K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}^{1}\right) .\right.} \\ \left.\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{ClO}^{1}\right)\right\}\left(\mathrm{P}\left(\mathrm{p}-\mathrm{tolyl} \mathrm{l}_{3}\right)\right] \mathrm{ClO}_{4} \\ (\text { at } 200 \mathrm{~K}) \end{gathered}$ | $\underset{\mathrm{P}_{4} / \mathrm{c}}{\mathrm{~m}}$ | $\begin{aligned} & 12.614(14) \\ & 20.280(20) \\ & 1.972(17) \end{aligned}$ | 98.96(1) | $\begin{gathered} \mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{P} \\ \mathrm{P}^{1} \mathrm{P}_{2} \mathrm{~N}^{1} \mathrm{C}^{3} \mathrm{O}^{0} 0.028 \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1} 2.21(1) \\ & \mathrm{N}^{1} 2.05(2) \\ & \mathrm{O}^{1} 2.03(2) \\ & \mathrm{LP} 2.269(1) \end{aligned}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 82.7 \\ \mathrm{~N}^{1}, \mathrm{O}^{1} 91.2 \\ \mathrm{P}^{1}, \mathrm{O}^{1} 172.1 \\ \mathrm{P}^{1}, \mathrm{P} 99.6 \\ \mathrm{O}^{1}, \mathrm{P} 86.5 \\ \mathrm{~N}^{1}, \mathrm{P} 177.7 \end{gathered}$ | $\begin{gathered} {[18]} \\ \text { KAVZOX } \end{gathered}$ |
| $\begin{gathered} {\left[\mathrm { Pt } \left\{\left(\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}^{1}\right) .\right.\right.\right.} \\ \left.\left(\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{OO}{ }^{1}\right)\right\} \\ (\mathrm{Cl})] \end{gathered}$ | $\mathrm{P}_{\mathrm{P}_{1} / \mathrm{n}}$ | $\begin{aligned} & 12.350(12) \\ & 12.138(14) \\ & 15.550(17) \end{aligned}$ | 97.70(1) | $\begin{gathered} \mathrm{Pttr}^{1} \mathrm{~N}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{Cll}^{1} \mathrm{~N}^{2} \mathrm{C}_{0} \mathrm{O}^{0.007} \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1} 2.195(1) \\ & \mathrm{N}^{1} 2.005(2) \\ & \mathrm{O}^{1} 2.080(2) \\ & \mathrm{Cl} 2.303(1) \end{aligned}$ | $\begin{gathered} \mathrm{P}^{1} \mathrm{~N}^{1} 83 . \mathrm{N}^{\mathrm{d}} \\ \mathrm{~N}^{1} \mathrm{~N}^{1} 92 . \mathrm{o}^{1} \\ \mathrm{P}^{1}, \mathrm{O}^{1} 178.5 \\ \mathrm{P}^{1}, \mathrm{Cl} 93.5 \\ \mathrm{O}^{1} \mathrm{Cl} 87.9 \\ \mathrm{~N}^{1}, \mathrm{Cl} 178.9 \end{gathered}$ | $\begin{gathered} { }^{[18]}{ }^{[18 Z A J} \end{gathered}$ |
| $\begin{aligned} & {\left[\mathrm{Ptt} \mathrm{~K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}^{1}\right) .\right.} \\ & \left.\left.\left(\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{OO}^{1}\right)\right\}(\mathrm{I})\right]\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) \end{aligned}$ | $\underset{\mathrm{P}_{4}{ }_{4} / \mathrm{c}}{\mathrm{~m}}$ | $\begin{aligned} & 10.446(11) \\ & 16.389(17) \\ & 16.507(0) \end{aligned}$ | 100.241(1) | $\begin{gathered} \mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{I} \\ \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{O}^{0} \mathrm{O}^{0.014} \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.207(1) \\ \mathrm{N}^{1} 2.011(2) \\ \mathrm{O}^{1} 2.045(2) \\ \mathrm{I} 2.620(1) \end{gathered}$ | $\mathrm{P}^{1}, \mathrm{~N}^{1} 84.8^{\mathrm{d}}$ <br> $\mathrm{N}^{1}, \mathrm{O}^{1} 91.9^{\mathrm{e}}$ <br> $\mathrm{P}^{1}, \mathrm{O}^{1} 176.6$ <br> $\mathrm{P}^{1}$, 192.6 <br> $\mathrm{O}^{1}$, I 89.2 <br> $\mathrm{N}^{1}, \mathrm{I} 178.2$ | ${ }_{\text {KAVZEN }}^{[18]}$ |
| $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{~N}^{1} \mathrm{O}^{1}\right)\right\}(\mathrm{Cl})\right]$ | $\underset{4}{\mathrm{or}} \underset{\mathrm{Pna}_{1}}{\mathrm{P}}$ | $\begin{aligned} & 18.88(2) \\ & 13.10(1) \\ & 9.66(1) \end{aligned}$ |  | $\begin{aligned} & \mathrm{Pttp}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{Cl}_{1}^{\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{2} \mathrm{C}^{1}} \\ & 0.027 \end{aligned}$ | $\begin{aligned} & \mathrm{P}^{1} 2.206(1) \\ & \mathrm{N}^{1} 1.88(1) \\ & \mathrm{O}^{1} 2.14(1) \\ & \mathrm{Cl} 2.386(4) \end{aligned}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 94.8(4){ }^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{O}^{9} 193.3(4){ }^{\mathrm{e}} \\ \mathrm{P}^{1}, \mathrm{O}^{1} 175.5 \\ \mathrm{P}^{1}, \mathrm{Cl} 89.1(2) \\ \mathrm{O}^{1}, \mathrm{Cl} 84.0(2) \\ \mathrm{N}^{1}, \mathrm{Cl} 174.8 \end{gathered}$ | $\begin{gathered} {[19]} \\ \text { DERNIX } \end{gathered}$ |
| C: $\operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{C}^{1}\right)(\mathrm{Y})$ |  |  |  |  |  |  |  |
| $\begin{gathered} {\left[\mathrm{Pt} \mid \mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}=\mathrm{NC} .\right.\right.} \\ \left.\left.\mathrm{C}^{1} \mathrm{C}_{5} \mathrm{H}_{6}\right)(\mathrm{Cl})\right] \\ (\mathrm{at} 120 \mathrm{~K})] \end{gathered}$ | $\underset{4}{\mathrm{P}_{1} / \mathrm{n}}$ | $\begin{aligned} & 8.632(4) \\ & 17.191(8) \\ & 15.216(7) \end{aligned}$ | 96.3(0) | $\begin{aligned} & \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{C}^{1} \mathrm{Cl}_{1}^{\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{\mathrm{N}} \mathrm{NCC}^{1}} \\ & 0.060 \end{aligned}$ | $\begin{aligned} & \mathrm{P}^{1} 2.291(2) \\ & \mathrm{N}^{1} 1.972(2) \\ & \mathrm{C}^{1} 2.023(2) \\ & \mathrm{Cl} 2.309(1) \end{aligned}$ | $\begin{gathered} \mathrm{P}^{1}, \mathrm{~N}^{1} 85.2^{\mathrm{d}} \\ \mathrm{~N}^{1}, \mathrm{C}^{1} 78 . \mathrm{C}^{\mathrm{d}} \\ \mathrm{P}^{1} \mathrm{C}^{1} 163.9 \\ \mathrm{P}^{1}, \mathrm{Cl} 99.9 \\ \mathrm{C}^{1}, \mathrm{Cl} 84.0 \\ \mathrm{~N}^{1}, \mathrm{Cl} 174.6 \end{gathered}$ | [20] YEHMOP |
| $\begin{gathered} {\left[\mathrm{Ptt} \mathrm{~K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right) .\right.} \\ \left.\left.\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{C}^{1}\right)\right\}\left(\mathrm{p}_{7}\right)\right] \mathrm{BF}_{4} \\ (\text { at } 100 \mathrm{~K}) \end{gathered}$ | $\underset{\substack{\mathrm{P} 2_{1} \\ 4}}{ }$ | $\begin{aligned} & 9.356(0) \\ & 19.892(1) \\ & 15.084(1) \end{aligned}$ | 90.76(0) | $\begin{gathered} \mathrm{Ptp}^{1} \mathrm{~N}^{1} \mathrm{C}^{1} \mathrm{~N}^{1}{ }^{1} \mathrm{C}_{3} \mathrm{~N}^{2} \mathrm{C}_{2} \\ 0.044 \end{gathered}$ | $\begin{gathered} \mathrm{P}^{1} 2.292(1) \\ \mathrm{N}^{1} 2.000(2) \\ \mathrm{C}^{1} 2.035(2) \\ \operatorname{pyN} 2.026(1) \end{gathered}$ | $\mathrm{P}^{1} \mathrm{~N}^{1} 92.1^{\mathrm{e}}$ <br> $\mathrm{N}^{1}, \mathrm{C}^{1} 82.3^{\mathrm{d}}$ <br> $\mathrm{P}^{1}, \mathrm{C}^{1} 174.3$ <br> $\mathrm{P}^{1}$, N 92.4 <br> $\mathrm{C}^{1}$, N 93.6 <br> $\mathrm{N}^{1}$,C1170.7 | $\begin{gathered} {[21]} \\ \text { NIVCAX } \end{gathered}$ |
| $\mathrm{D}: \operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1}\right)(\mathrm{Y})$ |  |  |  |  |  |  |  |
| $\begin{gathered} {\left[\mathrm{Pt} \mid \mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{CHN}^{1} \mathrm{NC}^{2} .\right.\right.} \\ \left.\left.\left(\mathrm{S}^{1}\right) \mathrm{NHMM}\right)(\mathrm{Cl})\right] \end{gathered}$ | $\mathrm{P}_{\mathrm{P}_{2} / \mathrm{c}}^{\mathrm{m}}$ | $\begin{aligned} & 14.695(6) \\ & 16.683(7) \\ & 19.297(9) \end{aligned}$ | 102.83(6) | $\begin{gathered} \mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1} \mathrm{Cl}_{1}^{\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{-} \mathrm{NCS}^{1}} \\ 0.022 \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1} 2.239(5) \\ & \mathrm{N}^{1} 2.03(2) \\ & \mathrm{s}^{1} 2.298(5) \\ & \mathrm{Cl} 2.304(5) \end{aligned}$ | $\begin{gathered} \hline \mathrm{P}^{1}, \mathrm{~N}^{1} 95.8(4)^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{~S}^{1} 84.9(4)^{\mathrm{d}} \\ \mathrm{P}^{1}, \mathrm{~S}^{1} 177.8(2) \\ \mathrm{P}^{1}, \mathrm{Cl} 89.5(2) \\ \mathrm{S}^{1}, \mathrm{Cl} 89.8(2) \\ \mathrm{N}^{1}, \mathrm{Cl} 174.4(4) \end{gathered}$ | [22] <br> HAFMOQ |
| $\begin{gathered} {\left[\mathrm{Pt}^{\left[\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{MeS}^{1}\right) .\right.}\right.} \\ \left.\left.\left(\mathrm{Bu}^{-} \mathrm{NH}_{2}\right)\right)(\mathrm{I})\right] \end{gathered}$ | $\begin{gathered} \mathrm{tr}_{\mathrm{P} 1} \\ 2 \end{gathered}$ | $\begin{aligned} & 10.529(1) \\ & 11.558(1) \\ & 14.550(1) \end{aligned}$ | $\begin{aligned} & 77.37(1) \\ & 84.45(1) \\ & 79.72(1) \end{aligned}$ |  | $\begin{gathered} \mathrm{P}^{1} 2.240(2) \\ \mathrm{N}^{1} 2.056(6) \\ \mathrm{S}^{1} 2.363(2) \\ \mathrm{I}^{1} 2.580(1) \end{gathered}$ | $\begin{gathered} \hline \mathrm{P}^{1}, \mathrm{~N}^{1} 89.1(1)^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{~S}^{1} 93.2(1)^{\mathrm{e}} \\ \mathrm{P}^{1}, \mathrm{~S}^{1} 176.2(2) \\ \mathrm{P}^{1}, \mathrm{I} 93.6(2) \\ \mathrm{S}^{1}, \mathrm{I} 84.2(2) \\ \mathrm{N}^{1}, \mathrm{I} 175.4(2) \end{gathered}$ | [23] <br> ROBHOP |

Table 1. Cont.

| Complex | Space gr. Cryst. cl. Z | $\begin{aligned} & \mathrm{a}[\mathrm{~A}] \\ & \mathrm{b}[\AA \mathrm{~A}] \\ & \mathrm{c}[\AA \mathrm{~A}] \end{aligned}$ | $\begin{aligned} & \left.\alpha\left[{ }^{\circ}\right]{ }^{\circ}{ }^{\circ}{ }^{\circ}{ }_{\gamma[ }\right] \end{aligned}$ | Chromophore (Chelate Rings) $\mathrm{T}_{4}{ }^{\mathrm{b}}$ | $\underset{\text { Pt-L }}{\substack{\text { c } \\ \hline}}$ | $\underset{\substack{\text { L-Pt-L" } \\\left[^{\mathrm{c}}\right]}}{ }$ | $\begin{aligned} & \text { Ref. } \\ & \text { REFCODE } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| E: Pt $\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{Se}^{1}\right)(\mathrm{Cl})$ |  |  |  |  |  |  |  |
| $\begin{aligned} & {\left[\mathrm{Ptt} \mathrm{~K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right) .\right.} \\ & \left(\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{Se}^{1}\right)\left(\mathrm{Phh}^{(\mathrm{CP})(\mathrm{Cl})] \mathrm{BF}_{4}}\right. \\ & (\text { at } 150 \mathrm{~K}) \end{aligned}$ | $\mathrm{P}_{2} \mathrm{~m}_{4} / \mathrm{c}$ | $\begin{aligned} & 9.869(0) \\ & 23.847(0) \\ & 11.740(0) \end{aligned}$ | 99.65(0) |  | $\begin{gathered} \mathrm{P}^{1} 2.407(14) \\ \mathrm{N}^{1} 2.028(4) \\ \mathrm{Se}^{1} 2.489(1) \\ \mathrm{Cl} 2.308(1) \end{gathered}$ | $\begin{gathered} \hline \mathrm{P}^{1}, \mathrm{~N}^{1} 87.5(1)^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{Se}^{1}{ }^{1} 95.7(1){ }^{\mathrm{e}} \\ \mathrm{P}^{1}, \mathrm{Se}^{1} 176.7(1) \\ \mathrm{P}^{1}, \mathrm{Cl} 93.0(1) \\ \mathrm{Se}^{1}, \mathrm{Cl} 83.7(1) \\ \mathrm{N}^{1}, \mathrm{Cl} 178.8(1) \end{gathered}$ | $\begin{gathered} {[24]} \\ \text { MULZIC } \end{gathered}$ |

Footnotes: ${ }^{\text {a }}$ 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. ${ }^{\text {b }}$ Parameter $\mathrm{T}_{4}$, degree of distortion. ${ }^{\mathrm{c}}$ The chemical identity of the coordinated atom ligand is specific in these columns. ${ }^{\text {d }}$ Five-membered metallocyclic ring. ${ }^{\text {e }}$ Six-membered metallocyclic ring.

In following six complexes: triclinic $\left.\left[\mathrm{Pt}_{\{1} \kappa^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right) \mathrm{N}^{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OH}\right)\right\}\left(\mathrm{CH}_{3}\right)\right]$. $\mathrm{CHCl}_{3}$ (at 150 K$)$ [11], monoclinic $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right) \mathrm{N}^{2}\left(\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{OH}\right)\right\}\left(\mathrm{CH}_{3}\right)\right]$.1.5toluene (at 150 K ) [11] $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{3} \mathrm{H}_{6}\right) \mathrm{N}^{2}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] .2$ toluene (at 150 K ) [11], monoclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{N}^{2}\left(\mathrm{C}_{10} \mathrm{H}_{9} \mathrm{NO}_{3}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] . \mathrm{Et}_{2} \mathrm{O}$ (at 150 K ) [12], monoclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{5} \mathrm{H}_{7} \mathrm{O}\right) \mathrm{N}^{2}\left(\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{~N}_{2}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] . \mathrm{H}_{2} \mathrm{O}$ (at 93 K$)$ [13], and monoclinic $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}\right) \mathrm{N}^{2}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OH}\right)\right\}\left(\mathrm{CH}_{3}\right)\right] . \mathrm{CHCl}_{3}$ (at 150 K ) [14] each $\kappa^{3}-P^{1} N^{1} N^{2}$ ligand creates six- and five-metallocyclic rings with the centre common ligating $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2}$ type. In each complex the methyl group completed a distorted square-planar geometry about each $\mathrm{Pt}(\mathrm{II})$ atom. The mean values for the respective chelate rings are: $93.8( \pm 4.0)^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $80.3( \pm 1.2)^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The remaining L-Pt-L bind angles open in the sequence (mean values): 90.9(1.9) ${ }^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{C}\right)<94.4(2.2)^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{C}\right)<$ $173.4(1.3)^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{C}\right)<173.7(4.7)^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The $\mathrm{Pt}-\mathrm{L}$ bond distance elongates in the order (mean values): $2.060( \pm 23) \AA\left(\mathrm{Pt}-\mathrm{C}\right.$, trans to $\left.\mathrm{N}^{1}\right)<2.066( \pm 21) \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to C$)<$ $2.079( \pm 15) \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.186( \pm 7) \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$, trans to $\left.\mathrm{N}^{2}\right)$.

The structure of the triclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{~N}^{2}\right)\right\}(\mathrm{Cl})\right]$ (at 150 K ) is shown in Figure 1, as an example [15]. As can be seen, the $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}$ ligand forms sixand five-membered metallocyclic rings of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCN}^{2}$ type with the centre common ligating $\mathrm{N}^{1}$ atom. The chlorido ligand completed a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The values of the respective rings are $95.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $79.3^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The remaining bind angles open in the sequence: $90.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<94.2^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<$ $173.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)<173.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$. The Pt-L bond distance elongates in the order: $2.053 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<2.086 \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.200 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.297 \AA$ ( $\mathrm{Pt}-\mathrm{Cl}$ ).

In the monoclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{~N}\right)\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{~N}^{2}\right)\right\}(\mathrm{Cl})\right] . \mathrm{PF}_{6}[16]$ the $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}$ ligand creates two six-membered metallocyclic rings with the centre common ligating $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{~N}^{2}$ type. The values of the chelate rings are $93.3^{\circ}$ (P1-Pt-N1) and $85.6^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The remaining bind angles open in the order: $90.9^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<91.8^{\circ}$ $\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<174.0^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<178.7^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The Pt-L bond distance elongates in the order: $2.104 \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.120 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<2.234 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<$ $2.284 \AA(\mathrm{Pt}-\mathrm{Cl})$.

## 2.2. $\operatorname{Pt}\left(\kappa^{3}-P^{1} N^{1} O^{1}\right)(Y)$ Derivatives

Structural data for five $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}\right)(\mathrm{Y})$ derivatives are gathered in Table $1\left(\mathrm{~B}: \operatorname{Pt}\left(\mathrm{K}^{3}-\right.\right.$ $\left.\left.\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}\right)(\mathrm{Y})\right)$. In the triclinic $\left[\mathrm{Pt}\left\{\kappa^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{~N}^{1}\right)\left(\mathrm{NC}_{7} \mathrm{H}_{5} \mathrm{O}^{1}\right)\right\}\left\{\kappa^{1}-\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{~N}_{2} \mathrm{O}\right)\right\}\right] . \mathrm{CH}_{2} \mathrm{Cl}_{2}$ (at 200 K ) [17] the $\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ ligand with monodentate PL donor ligand builds up a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom ( $\mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{O}^{1} \mathrm{P}$ ). The $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ ligand forms two five-membered metallocyclic rings with the centre common ligating $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{NCO}^{1}$ type, with the values of the chelate rings of $83.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $78.8^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)$. The remaining L-Pt-L bind angles open in the sequence: $94.7^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{P}\right)<$ $102.9^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{P}\right)<162.4^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)<173.3^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{P}\right)$. The Pt-L bond distance elongates
in the order: $1.985 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to P$)<2.050 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.233 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<$ $2.261 \AA(\mathrm{Pt}-\mathrm{P})$.


Figure 1. Structure of $\left[\operatorname{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}\right)\left(\mathrm{NC}_{5} \mathrm{H}_{5} \mathrm{~N}^{2}\right)\right\}(\mathrm{Cl})\right]$ [15].
In the monoclinic $\left[\mathrm{Pt}\left\{\kappa^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{ClO}^{1}\right)\right\}\left\{\mathrm{P}(\mathrm{p} \text {-tolyl) })_{3}\right\}\right] . \mathrm{ClO}_{4}$ (at 200 K$)$ [18] a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom is built up by the $\mathrm{k}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ ligand with $\mathrm{P}(\mathrm{p} \text {-tolyl })_{3}$. The $\mathrm{\kappa}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ ligand forms five- and six-membered metallocyclic rings with the common $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{1}$ type with the values of the chelate rings of $82.7^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $91.2^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $86.5^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{P}\right)<99.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{P}\right)<172.1^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)<177.7^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{P}\right)$. The Pt-L bond distance elongates in the order: $2.03 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$ trans to $\left.\mathrm{P}^{1}\right)<2.05 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$ trans to P$)<2.21(1) \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.269 \AA(\mathrm{Pt}-\mathrm{P})$.

Two monoclinics $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{OO}^{1}\right)\right\}(\mathrm{Z})\right](\mathrm{Z}=\mathrm{Cl}$ or I) are isostructural [18]. The $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ with Z builds up distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atoms. The values of $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{1}$ metallocyclic rings are $83.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $92.3^{\circ}$ ( $\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{1}$ ) when $\mathrm{Z}=\mathrm{Cl}$; for $\mathrm{Z}=\mathrm{I}$, the values are $84.8^{\circ}$ and $91.9^{\circ}$, respectively. The remaining L-Pt-L bind angles open in the order: $87.9^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<93.5^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<178.5^{\circ}$ $\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)<178.9^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$; vs. $89.2^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{I}\right)<92.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{I}\right)<176.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)<$ $178.2^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{I}\right)$. As can be seen, the L-Pt-L angles for $\mathrm{Cl}^{-}$complex are somewhat larger than for $\mathrm{I}^{-}$complex, except $\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{X}$. The Pt-L bond distance elongates in the order: $2.005 \AA$ $\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<2.080 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.195 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.303 \AA(\mathrm{Pt}-\mathrm{Cl}) ;$ vs. $2.011 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to I$)<2.045 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.207 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.620 \AA(\mathrm{Pt}-\mathrm{I})$.

In orthorhombic $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{~N}^{1} \mathrm{O}^{1}\right)\right\}(\mathrm{Cl})\right][19]$, the $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}$ ligand form two six-membered metallocyclic rings of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{1}$ type with the central common ligating $\mathrm{N}^{1}$ atom. The clorido ligands completed a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The values of the chelate rings are $94.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $93.3^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $84.0^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<89.1^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$ $<174.8^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<175.5^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}^{1}\right)$. The $\mathrm{Pt}-\mathrm{L}$ bond distance elongates in the order: $1.88 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<2.14 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.206 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.386 \AA(\mathrm{Pt}-\mathrm{Cl})$.

## 2.3. $\operatorname{Pt}\left(\kappa^{3}-P^{1} N^{1} C^{1}\right)(Y)$ Derivatives

There are two monoclinic complexes $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}=\mathrm{NCC}^{1} \mathrm{C}_{5} \mathrm{H}_{6}\right)\right\}(\mathrm{Cl})\right]$ (Figure 2) (at 120 K ) [20] and $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{C}^{1}\right)\right\}(\mathrm{py})\right] . \mathrm{BF}_{4}$ (at 100 K ) [21] (Table 1 (C: $\left.\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{C}^{1}\right)(Y)\right)$ ). In the former complex, the $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{C}^{1}$ ligand forms two fivemembered metallocyclic rings of the $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{NCC}^{1}$ type, with the values of the chelate rings of $85.2^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $78.7^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{C}^{1}\right)$, respectively. The clorido ligands completed a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The remaining L-Pt-L bind angles open in the order: $84.0^{\circ}\left(\mathrm{C}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<99.9^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<163.9^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{C}^{1}\right)<174.6^{\circ}$ $\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$. The Pt-L bond distance elongates in the order: $1.972 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<$ $2.023 \AA\left(\mathrm{Pt}-\mathrm{C}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.291 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.309 \AA(\mathrm{Pt}-\mathrm{Cl})$.


Figure 2. Structure of $\left[\operatorname{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}=\mathrm{NCC}^{1} \mathrm{C}_{5} \mathrm{H}_{6}\right)\right\}(\mathrm{Cl})\right]$ [20].
In the complex cation, the N -donor atom of pyridine completed the inner coordination sphere about the $\operatorname{Pt}(\mathrm{II})$ atom $\left(\mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{C}^{1} \mathrm{~N}\right)$. The $\mathrm{K}^{3}$-ligand creates six- and five-membered metallocycles of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{C}^{1}$ type. The values of the respective chelate rings are $92.1^{\circ}$ $\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $82.3^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{C}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $92.4^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}\right)<93.6^{\circ}\left(\mathrm{C}^{1}-\mathrm{Pt}-\mathrm{N}\right)<170.7^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<174.3^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{C}^{1}\right)$. The Pt-L bond distance elongates in the order: $2.000 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$ trans to N$)<2.026 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right)<2.035 \AA$ $\left(\mathrm{Pt}-\mathrm{C}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.292 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)$.

## 2.4. $\operatorname{Pt}\left(\mathcal{K}^{3}-P^{1} N^{1} S^{1}\right)(Y)$ Derivatives

There are two such derivatives, monoclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{CHN}{ }^{1} \mathrm{NC}\left(\mathrm{S}^{1}\right) \mathrm{NHMe}\right\}\right.\right.$ $(\mathrm{Cl})][22]$ and triclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{MeS}^{1}\right)\left(\mathrm{Bu}^{\mathrm{t}} \mathrm{NH}_{2}\right)\right\}(\mathrm{I})\right]$ [23] (Table 1 (D: $\mathrm{Pt}\left(\mathrm{k}^{3}-\right.$ $\left.P^{1} N^{1} S^{1}\right)(Y)$ )). In the monoclinic complex, the $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1}$ ligand with chlorido builds up distorted square-planar geometry about the $\operatorname{Pt}(\mathrm{II})$ atom. The $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1}$ ligand in the chlorido complex creates six- and five-membered metallocyclic rings with the centre common ligating $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}$ type. The values of the chelate rings are $95.8^{\circ}$ ( $\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}$ ) and $84.9^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $89.5^{\circ}$ $\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<89.8^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<174.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<177.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. The $\mathrm{Pt}-\mathrm{L}$ bond distance elongates in the order: $2.03 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<2.239 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$, trans to $\left.\mathrm{S}^{1}\right)<$ $2.298 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<2.304 \AA(\mathrm{Pt}-\mathrm{Cl})$.

In the triclinic complex, the $\kappa^{3}-P^{1} N^{1} S^{1}$ ligand creates two six-membered metallocyclic rings of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{~S}^{1}$ type with the values of the chelate rings of $89.1^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and
$93.2^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $84.2^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{I}\right)<$ $93.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{I}\right)<175.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{I}\right)<176.2^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. The Pt-L bond distance elongates in the order: $2.056 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to I$)<2.240 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$, trans to $\left.\mathrm{S}^{1}\right)<2.363 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<$ $2.580 \AA$ ( $\mathrm{Pt}-\mathrm{I}$ ).

## 2.5. $\operatorname{Pt}\left(\kappa^{3}-P^{1} N^{1} S e^{1}\right)(Y)$ Derivatives

Monoclinic $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{~N}^{1}\right)\left(\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{Se}^{1}\right)(\mathrm{Ph})\right\}(\mathrm{Cl})\right] \cdot \mathrm{BF}_{4}$ (at 150 K$)$ [24] is the only example of $\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{Se}^{1}$ type. The $\mathrm{Cl}^{-}$anion completed a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The $\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{Se}^{1}$ ligand creates two six-membered metallocyclic rings with the centre common ligating $\mathrm{N}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{Se}^{1}$ type. The values of the chelate rings are $87.5^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $95.7^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Se}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $83.7^{\circ}\left(\mathrm{Se}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<93.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<176.7^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Se}^{1}\right)<178.8^{\circ}$ $\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$. The $\mathrm{Pt}-\mathrm{L}$ bond distance elongates in the order: $2.028 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to Cl$)<$ $2.308 \AA(\mathrm{Pt}-\mathrm{Cl})<2.407 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$, trans to $\left.\mathrm{Se}^{1}\right)<2.489 \AA\left(\mathrm{Pt}-\mathrm{Se}^{1}\right)$.

## 2.6. $\operatorname{Pt}\left(\kappa^{3}-N^{1} P^{1} N^{2}\right)(C l)$ and $P t\left(\kappa^{3}-S^{1} P^{1} S^{2}\right)(C l)$ Derivatives

Their structural data are gathered in Table 2. In orthorhombic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{N}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{10}\right)\right.\right.$ $\left.\left.\mathrm{NP}^{1}\left(\operatorname{Pr}^{\mathrm{i}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}^{2}\right\}(\mathrm{Cl})\right] \mathrm{Cl} . \mathrm{H}_{2} \mathrm{O}$ (at 150 K$)[25]$ heterotridentate $\mathrm{K}^{3}-\mathrm{N}^{1} \mathrm{P}^{1} \mathrm{~N}^{2}$ ligand with $\mathrm{Cl}^{-}$ anion builds up a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The $\kappa^{3}-\mathrm{N}^{1} \mathrm{P}^{1} \mathrm{~N}^{2}$ ligand forms two six-membered metallocyclic rings with the centre common ligating $\mathrm{P}^{1}$ atom of the $\mathrm{N}^{1} \mathrm{C}_{2} \mathrm{NP}^{1} \mathrm{NC}_{2} \mathrm{~N}^{2}$ type. The values of the chelate rings are: $91.1^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{P}^{1}\right)$ and $91.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The remaining L-Pt-L bind angles open in the order: $90.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<$ $91.0^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<173.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<175.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right)$. The Pt-L bond distance elongates in the order: $2.035 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to $\left.\mathrm{N}^{2}\right)<2.039 \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right)<2.187 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$. trans to Cl$)<$ $2.375 \AA(\mathrm{Pt}-\mathrm{Cl})$.

Table 2. Data for $\operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{X}^{1} \mathrm{P}^{1} \mathrm{X}^{2}\right)(\mathrm{Cl}), \operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}\right)(\mathrm{Cl})$ and $\operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}\right)(\mathrm{OL})$ derivatives monodentate atoms/ligands) ${ }^{\text {a }}$.

| Complex | Space gr. Cryst. cl. Z | $\begin{aligned} & \mathrm{a}[\mathrm{~A}] \\ & \mathrm{b}[\AA \mathrm{~A}] \\ & \mathrm{c}[\AA \mathrm{~A}] \end{aligned}$ | $\begin{aligned} & \alpha\left[{ }^{\circ}\right] \\ & \beta\left[{ }^{\circ}\right] \\ & \gamma\left[{ }^{\circ}\right] \end{aligned}$ | Chromophore (Chelate Rings) $\mathrm{T}_{4}{ }^{\mathrm{b}}$ | $\underset{[A]}{P t-L{ }^{c}}$ | $\begin{aligned} & \mathrm{L}-\mathrm{Pt}-\mathrm{L}^{\mathrm{c}} \\ & \mathrm{C}^{\circ} \end{aligned}$ | $\begin{aligned} & \text { Ref. } \\ & \text { REFCODE } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} {\left[\mathrm{Ptt} \mathrm{~K}^{3}-\mathrm{N}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{10}\right) \mathrm{N} . .\right.} \\ \left.\left.\mathrm{P}^{1}\left(\mathrm{Pr}^{1}\right)\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}^{2}\right)(\mathrm{Cl})\right] \cdot \mathrm{H}_{2} \mathrm{O} \\ (\mathrm{at} 150 \mathrm{~K}) \end{gathered}$ | $\underset{{ }_{6} 2_{1}}{\stackrel{\text { or }}{2} 2_{1}}$ | $\begin{aligned} & 14.373(0) \\ & 9.906(0) \\ & 17.590(0) \end{aligned}$ |  | $\begin{gathered} \mathrm{PtN}^{1} \mathrm{P}^{1} \mathrm{~N}^{2} \mathrm{Cl} \\ \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{NP}^{1} \mathrm{Na}^{-\mathrm{NC}_{2}} \mathrm{~N}^{2} \end{gathered}$ | $\begin{aligned} & \mathrm{N}^{1}{ }^{1} 2.035 \\ & \mathrm{P}^{1} 2.187 \\ & \mathrm{~N}^{2} 2.239 \\ & \mathrm{Cl} 2.375 \end{aligned}$ | $\begin{aligned} & \mathrm{N}^{1}, \mathrm{P}^{1} 91.1^{\mathrm{e}} \\ & \mathrm{P}^{1} \mathrm{~N}^{2} 91 . \mathrm{e}^{\mathrm{e}} \\ & \mathrm{~N}^{1}, \mathrm{~N}^{2} 175.4 \\ & \mathrm{~N}^{1}, \mathrm{Cl} 90.4 \\ & \mathrm{~N}^{2}, \mathrm{Cl} 91.0 \\ & \mathrm{P}^{1}, \mathrm{Cl} 173.0 \end{aligned}$ | $\begin{gathered} {[25]} \\ \text { IRAWOO } \end{gathered}$ |
|  | $\mathrm{P}_{\mathrm{P}_{1} / \mathrm{n}}$ | $\begin{aligned} & 8.790(0) \\ & 18.706(1) \\ & 15.508(1) \end{aligned}$ | 95.89(0) | $\begin{gathered} \mathrm{P}^{\mathrm{P} 5^{1} \mathrm{P}^{1} \mathrm{~S}^{2} \mathrm{Cl}} \\ \mathrm{~S}^{1} \mathrm{C}_{2} \mathrm{P}^{2} \mathrm{C}_{2} \mathrm{~S}^{0.055} \end{gathered}$ | $\begin{aligned} & \mathrm{S}^{1} 2.289 \\ & \mathrm{P}^{1} 2.189 \\ & \mathrm{~S}^{2} 2.292 \\ & \mathrm{Cl} 2.374 \end{aligned}$ | $\begin{aligned} & \mathrm{S}^{1}, \mathrm{P}^{1} 88.2^{\mathrm{d}} \\ & \mathrm{P}^{1} \mathrm{~S}^{2} 88.7^{\mathrm{d}} \\ & \mathrm{~S}^{1} \mathrm{~S}^{2} 162.1 \\ & \mathrm{~S}^{1}, \mathrm{Cl} 93.0 \\ & \mathrm{~S}^{2}, \mathrm{Cl} 90.8 \\ & \mathrm{P}^{1}, \mathrm{Cl} 178.3 \end{aligned}$ | [26] <br> EZORAO |
| $\begin{gathered} {\left[\mathrm { Pt } \left\{\mathrm{K}^{3}-\mathrm{Bu}^{\mathrm{t}} \mathrm{~S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1} .\right.\right.} \\ \left.\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SBu} \mathrm{Su}^{\mathrm{t}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right]\left(\mathrm{Cl)]} \cdot 0.5 \mathrm{CHCl}_{3}\right. \\ \left(\mathrm{at}_{123} \mathrm{~K}\right) \end{gathered}$ | $\mathrm{P}_{\mathrm{P}_{4} / \mathrm{n}}$ | $\begin{aligned} & 10.250(1) \\ & 18.715(2) \\ & 15.320(1) \end{aligned}$ | 96.65(0) | $\begin{gathered} \mathrm{P}^{\mathrm{P} S^{1} \mathrm{P}^{1} \mathrm{~S}^{2} \mathrm{Cl}^{1}} \mathrm{~S}^{1} \mathrm{C}_{2} \mathrm{P}^{2} \mathrm{C}^{2} \mathrm{~S}^{0.063} \end{gathered}$ | $\begin{aligned} & \mathrm{S}^{1} 2.287 \\ & \mathrm{P}^{1} 2.288 \\ & \mathrm{~S}^{2} 2.297 \\ & \mathrm{Cl}^{2} 2.360 \end{aligned}$ | $\begin{aligned} & \mathrm{S}^{1}, \mathrm{P}^{1} 88.7 \mathrm{P}^{\mathrm{d}} \\ & \mathrm{P}^{1}, \mathrm{~S}^{2} 88.8 \\ & \mathrm{~S}^{1}, \mathrm{~S}^{2} 158.7 \\ & \mathrm{~N}^{1}, \mathrm{Cl} 92.8 \\ & \mathrm{~N}^{2}, \mathrm{Cl} 9.8 \\ & \mathrm{P}^{1}, \mathrm{Cl} 178.8 \end{aligned}$ | $\begin{gathered} {[26]} \\ \text { EZOQIV } \end{gathered}$ |
|  | $\begin{gathered} \text { or } \\ \mathrm{Pna}_{4} \\ 4 \end{gathered}$ | $\begin{aligned} & 21.373(0) \\ & 8.959(0) \\ & 25.330(3) \end{aligned}$ |  | $\begin{gathered} \mathrm{Ptpl}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1} \mathrm{Cl} \\ \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~S}^{\mathrm{S}} \mathrm{C}_{2} \mathrm{BCCl} \\ 0.033 \end{gathered}$ | $\begin{aligned} & \mathrm{P}^{1}{ }^{1} 2.212 \\ & \mathrm{~S}^{1} 2.243 \\ & \mathrm{Cl}^{1} 2.2431 \\ & \mathrm{Cl}^{2} 2.321 \end{aligned}$ | $\mathrm{P}^{1}, \mathrm{~S}^{1} 87.9^{\mathrm{d}}$ <br> $\mathrm{S}^{1}, \mathrm{Cl}^{1} 87.1^{\mathrm{e}}$ <br> $\mathrm{P}^{1}, \mathrm{Cl}^{1} 174.7$ <br> $\mathrm{P}^{1}$, Cl 93.4 <br> $\mathrm{Cl}^{1}, \mathrm{Cl} 91.7$ <br> S ${ }^{1}, \mathrm{Cl} 173.3$ | ${ }^{[27]} \text { DASMER }$ |
| $\begin{gathered} {\left[\mathrm { Pt } \left\{\mathrm{K}^{3}-\mathrm{cyh}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{Si}^{1} .\right.\right.} \\ \left.\left(\mathrm{CH}_{3}\right)\left(\begin{array}{c} 7 \\ \hline \end{array} \mathrm{H}_{6} \mathrm{~N}^{1}\left(\mathrm{CH}_{3}\right) 2\right)\right) . \\ \left.\left(\mathrm{SO}_{2} \mathrm{CF}_{3}\right)\right] \\ (\mathrm{at} 123 \mathrm{~K}) \end{gathered}$ | $\mathrm{P}_{\mathrm{P}_{4} / \mathrm{c}}^{\mathrm{m}}$ | $\begin{aligned} & 19.851(1) \\ & 20.837(3) \\ & 15.443(2) \end{aligned}$ | 99.52(0) | $\begin{gathered} \mathrm{PtP}^{\mathrm{Pt}^{1} \mathrm{Si}^{1} \mathrm{~N} \mathrm{~N}^{1} \mathrm{O}} \mathrm{P}^{1} \mathrm{C}_{2}^{1} \mathrm{~S}^{1} \mathrm{C}^{1} \mathrm{~N}^{0.033} \end{gathered}$ | $\begin{aligned} & \mathrm{Pl}^{1}{ }^{2} .228 \\ & \mathrm{Si}^{2} 2.260 \\ & \mathrm{~N}^{2} 2.177 \\ & \mathrm{LO}_{2}^{2.353} \end{aligned}$ | $\begin{gathered} \mathrm{P}^{1} \mathrm{Si}^{1} 85.8^{\mathrm{d}} \\ \mathrm{Si}^{\mathrm{d}} \mathrm{~N}^{1} \mathrm{~N}^{1} 82.7 \mathrm{e}^{\mathrm{P}} \\ \mathrm{P}^{1} \mathrm{~N}^{1} 169.2 \\ \mathrm{P}_{1}^{\mathrm{O}} 95.0 \\ \mathrm{~N}^{1}, \mathrm{O} 86.4 \\ \mathrm{Si}^{1}, \mathrm{O} 179.0 \end{gathered}$ | $\begin{gathered} {[28]} \\ \text { WUXFAI } \end{gathered}$ |

Footnotes: ${ }^{\text {a }}$ 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. ${ }^{\text {b }}$ Parameter $\mathrm{T}_{4}$, degree of distortion. ${ }^{\mathrm{c}}$ The chemical identity of the coordinated atom ligand is specific to these columns.
${ }^{\mathrm{d}}$ Six- membered metallocyclic ring. ${ }^{\text {e }}$ Five-membered metallocyclic ring.

Two monoclinic complexes $\left[\mathrm{Pt}\left\{\mathrm{k}^{3}-\operatorname{Pr}^{\mathrm{i}} \mathrm{S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SPr}^{\mathrm{i}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right\}(\mathrm{Cl})\right]$ (Figure 3) (at 123 K ) [26] and $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Bu}^{\mathrm{t}} \mathrm{S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SBu}^{\mathrm{t}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right\}(\mathrm{Cl})\right] .0 .5 \mathrm{CHCl}_{3}$ (at 123 K ) [26] have a similar structure. In each, the $\kappa^{3}-S^{1} P^{1} S^{2}$ ligand forms two five-membered metallocycles with the centre common ligating $\mathrm{P}^{1}$ atom of the $\mathrm{S}^{1} \mathrm{C}_{2} \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~S}^{2}$ type. In the former complex, the values of the chelate rings are $88.2^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{P}^{1}\right)$ and $87.7^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)$. The remaining L-Pt-L angles open in the order: $90.8^{\circ}\left(\mathrm{S}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<93.0^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<162.1^{\circ}\left(\mathrm{S}^{1}-\right.$ $\left.\mathrm{Pt}-\mathrm{S}^{2}\right)<178.3^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$. In the latter complex, the L-Pt-L angles open in the order: $88.7^{\circ}$ $\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{P}^{1}\right)<88.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)<90.8^{\circ}\left(\mathrm{S}^{2}-\mathrm{Pt}-\mathrm{Cl}\right)<158.7^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)<178.6^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)$.


Figure 3. Structure of $\left[\operatorname{Pt}\left\{\mathrm{K}^{3}-\operatorname{Pr}^{\mathrm{i}} \mathrm{S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \operatorname{SPr}^{\mathrm{i}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right\}(\mathrm{Cl})\right]$ [26].
The Pt-L bond distance elongates in the order (mean values): 2.194 $( \pm 4) \AA$ ( $\mathrm{Pt}-\mathrm{P}^{1}$, trans to Cl$)<2.288 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right.$ trans to $\left.\mathrm{S}^{2}\right)<2.294( \pm 3) \AA\left(\mathrm{Pt}-\mathrm{S}^{2}\right)<2.367( \pm 7) \AA(\mathrm{Pt}-\mathrm{Cl})$.

## 2.7. $\operatorname{Pt}\left(\kappa^{3}-P^{1} S^{1} C l^{1}\right)(C l)$ and $\operatorname{Pt}\left(\kappa^{3}-P^{1} S i^{1} N^{1}\right)(O L)$ Derivatives

Their structural data are given in Table 2. In the orthorhombic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{23} \mathrm{H}_{28} \mathrm{~S}^{1}\right)\right.\right.$ (B) $\left.\left.\left(\mathrm{Ph}_{2}\right) \mathrm{Cl}^{1}\right\}(\mathrm{Cl})\right] \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ (Figure 4) (at 123 K ) [27] heterotridentate $\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}$ ligand with the $\mathrm{Cl}^{-}$anion builds up a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The $\kappa^{3}-\mathrm{P}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}$ forms five- and six-metallocyclic rings of the $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~S}^{1} \mathrm{C}_{2} \mathrm{BCl}^{1}$ type. The values of the respective chelate rings are $87.9^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$ and $87.1^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}^{1}-\mathrm{Cl}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $91.7^{\circ}\left(\mathrm{Cl}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<93.4^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<173.3^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{Cl}\right)<$ $174.7^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Cl}^{1}\right)$. The Pt-L bond distance elongates in the order: $2.212 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right.$, trans to $\left.\mathrm{Cl}^{1}\right)<2.243 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right.$, trans to Cl$)<2.321 \AA(\mathrm{Pt}-\mathrm{Cl})<2.391 \AA\left(\mathrm{Pt}-\mathrm{Cl}^{1}\right)$.

Structure of the monoclinic $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{cyh}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{Si}^{1}\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{7} \mathrm{H}_{6}\right) \mathrm{N}^{1}\left(\mathrm{CH}_{3}\right)_{2}\right\}\left(\mathrm{OSO}_{2} \mathrm{CF}_{3}\right)\right]$ [28] is shown in Figure 5. The $\kappa^{3}-\mathrm{P}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}$ ligand with OL builds up a distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The chelate ligand forms five- and six-membered metallocyclic rings with the central common ligating $\mathrm{Si}^{1}$ atom of the $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{Si}^{1} \mathrm{C}_{3} \mathrm{~N}^{1}$ type. The values of the respective angles are $85.8^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{Si}^{1}\right)$ and $82.7^{\circ}\left(\mathrm{Si}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$. The remaining L-Pt-L bind angles open in the order: $86.4^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}\right)<95.0^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{O}\right)<169.2^{\circ}\left(\mathrm{P}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)<$
$179.0^{\circ}\left(\mathrm{Si}^{1}-\mathrm{Pt}-\mathrm{O}\right)$. The Pt-L bond distance elongates in the order: $2.177 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$, trans to $\left.\mathrm{P}^{1}\right)<2.228 \AA\left(\mathrm{Pt}-\mathrm{P}^{1}\right)<2.260 \AA\left(\mathrm{Pt}-\mathrm{Si}^{1}\right.$, trans to O$)<2.353 \AA(\mathrm{Pt}-\mathrm{O})$.


Figure 4. Structure of $\left.\mathrm{Pt}\left\{\mathrm{k}^{3}-\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{23} \mathrm{H}_{28} \mathrm{~S}^{1}\right)(\mathrm{B})\left(\mathrm{Ph}_{2}\right) \mathrm{Cl}^{1}\right\}(\mathrm{Cl})\right]$ [27].


Figure 5. Structure of $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-\mathrm{cyh}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{Si}^{1}\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{7} \mathrm{H}_{6}\right) \mathrm{N}^{1}\left(\mathrm{CH}_{3}\right)_{2}\right\}\left(\mathrm{OSO}_{2} \mathrm{CF}_{3}\right)\right]$ [28].

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 $\mathrm{Pt}(\mathrm{II})$ atoms. There are twenty four $\mathrm{Pt}(\mathrm{II})$ 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. $\quad 5+5$-membered: P1C2P1C2N2 (1 example), P1C2N1NCO1 (1 example), $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{NCC}^{1}$ (1 example) and $\mathrm{S}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~S}^{2}$ (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. $\quad 6+6$-membered: $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{~N}^{2}, \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{1}, \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{~S}^{1}, \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{Se}^{1}$ and $\mathrm{N}^{1} \mathrm{C}_{2} \mathrm{NP}^{1} \mathrm{NC}_{2} \mathrm{~N}^{2}$ (each 1 example)
In the $\operatorname{Pt}\left(\kappa^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{X}\right)(\mathrm{Y}),\left(\mathrm{X}=\mathrm{N}^{2}, \mathrm{O}^{1}, \mathrm{C}^{1}, \mathrm{~S}^{1}\right.$, or $\left.\mathrm{Se}^{1}\right)$ complexes (Table 1) the total mean values of Pt-L bind distance elongate in the sequences:

Pt- $\mathrm{P}^{1}$ (trans to X): $2.20 \AA\left(\mathrm{~N}^{2}\right)<2.22 \AA\left(\mathrm{O}^{1}\right)<2.23 \AA\left(\mathrm{C}^{1}\right)<2.24 \AA\left(\mathrm{~S}^{1}\right)<2.40 \AA\left(\mathrm{Se}^{1}\right)$;
Pt- $\mathrm{X}^{1}$ (trans to $\mathrm{P}^{1}$ ): $2.03 \AA\left(\mathrm{C}^{1}\right)<2.065 \AA\left(\mathrm{O}^{1}\right)<2.085 \AA\left(\mathrm{~N}^{2}\right)<2.330 \AA\left(\mathrm{~S}^{1}\right)<2.489 \AA\left(\mathrm{Se}^{1}\right)$;
Pt-N ${ }^{1}$ (trans to Y): $1.985 \AA\left(\mathrm{P}^{2}\right)<2.00 \AA\left(\mathrm{~N}^{3}\right)<2.02 \AA(\mathrm{Cl})<2.03 \AA(\mathrm{I})<2.065 \AA\left(\mathrm{C}^{2}\right)$;
Pt- $\mathrm{Y}^{1}\left(\right.$ trans to $\left.\mathrm{N}^{1}\right): 2.005 \AA\left(\mathrm{~N}^{3}\right)<2.068 \AA\left(\mathrm{C}^{2}\right)<2.260 \AA\left(\mathrm{P}^{2}\right)<2.304 \AA(\mathrm{Cl})<2.600 \AA(\mathrm{I})$.
These correspond quite were with the trans influence of the $X^{1}$ /ligand.

## 3. Conclusions

This review covers 24 monomeric four-coordinated $\mathrm{Pt}(\mathrm{II})$ complexes. The inner coordination sphere about the $\mathrm{Pt}(\mathrm{II})$ atoms are built up heterotridentate organomonophosphines with the monodentate atom/ligand. The $\kappa^{3}$-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
$\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{NCO}^{1} 83.6 / 78.8^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{NCC}^{1} 85.2 / 78.7^{\circ} ; \mathrm{S}^{1} \mathrm{C}_{2} \mathrm{P}^{1} / \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~S}^{2} 88.5 / 88.2^{\circ}$; $\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} 85.5 / 83.4^{\circ}$
$6+5$-membered
$\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{2} \mathrm{C}^{1} 92.1 / 82.3^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} 93.8 / 80.2^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{NCN}^{2} 94.5 / 82.5^{\circ} ;$ $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{NCS}^{1} 95.8 / 84.9^{\circ}$;
$5+6$ membered
$\mathrm{P}^{1} \mathrm{C}_{2} \mathrm{Si}^{1} / \mathrm{Si}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} 85.6 / 82.7^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~S}^{1} / \mathrm{S}^{1} \mathrm{C}_{2} \mathrm{BCl}^{1} 87.9 / 87.1^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{3} \mathrm{O}^{1} 83.7 / 91.8^{\circ}$
$6+6$ membered
$\mathrm{N}^{1} \mathrm{C}_{2} \mathrm{NP}^{1} / \mathrm{P}^{1} \mathrm{NC}_{2} \mathrm{~N}^{2} 91.1 / 91.0^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{3} \mathrm{O}^{1} 94.8 / 93.3^{\circ} ; \mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{3} \mathrm{~S}^{1} 89.1 / 93.2^{\circ} ;$ $\mathrm{P}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} / \mathrm{N}^{1} \mathrm{C}_{3} \mathrm{Se}^{1} 82.5 / 95.2^{\circ}$

It is well known that in four coordinates, $\mathrm{Pt}(\mathrm{II})$ 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- $\alpha$ - L-Pt-L (L are terminal ligating atoms of the respective chelate) and trans- $\beta-\mathrm{L}^{\prime}-\mathrm{Pt}-\mathrm{Y}$ ( $\mathrm{L}^{\prime}$ central ligating atom of the rings) bond angles and of $T_{4}$ are given in Table 3.

As can be seen (Table 3) where $\beta$-angles are almost constant, the $\alpha$-angles are mostly growing with the membered of the respective rings. The distortion of the square- planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atoms is diminishing.

Table 3. Summary of metallocyclic rings, trans-L-Pt-L angles and parameter $\mathrm{T}_{4}$.

| Metallocyclic Rings | $\boldsymbol{\alpha}$ - L-Pt-L <br> $\left[{ }^{\circ}\right]$ | $\boldsymbol{\beta}-$ L'$^{\prime}-\mathrm{Pt}-\mathrm{Y}$ <br> $\left[{ }^{\circ}{ }^{\boldsymbol{1}}\right.$ | $\mathrm{T}_{4}$ |
| :--- | :--- | :--- | :--- |
| $5+5-$ 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 $\mathrm{Pt}(\mathrm{II})$ atoms is diminishing in the order of the respective complexes (total mean values): $0.059\left(\mathrm{PtS}^{1} \mathrm{P}^{1} \mathrm{~S}^{2}\right)(\mathrm{Y})>0.051$ $\left(\mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{C}^{1}\right)(\mathrm{Y})>0.033\left(\mathrm{PtP}^{1} \mathrm{Si}^{1} \mathrm{~N}^{1}\right)(\mathrm{Y}) \sim 0.033\left(\mathrm{PtP}^{1} \mathrm{~S}^{1} \mathrm{Cl}^{1}\right)(\mathrm{Y})>0.032\left(\mathrm{PtN}^{1} \mathrm{P}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y})>0.028$ $\left(\operatorname{PtP}^{1} \mathrm{~N}^{1} \mathrm{O}^{1}\right)(\mathrm{Y})>0.023\left(\mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1}\right)(\mathrm{Y})>0.012\left(\mathrm{PtP}^{1} \mathrm{~N}^{1} \mathrm{Se}^{1}\right)(\mathrm{Y})$

Noticeably, in some complexes there is a relationship between the inner coordination sphere about the $\mathrm{Pt}(\mathrm{II})$ 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 $\mathrm{T}_{4}$. The (Pt-L(x4) vs. $\mathrm{T}_{4}$ ) are:

$$
\begin{aligned}
& \operatorname{Pt}\left(\mathrm{K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~N}^{2}\right)(\mathrm{Y}): 8.394 \AA \text { vs. } 0.036(\mathrm{Y}=\mathrm{CL}) ; 8.647 \AA \text { i̊. } 0.034(\mathrm{Y}=\mathrm{Cl}) \\
& \mathrm{Pt}\left(\mathrm{~K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{O}^{2}\right)(\mathrm{Y}): 8.556 \AA \text { vs. } 0.048(\mathrm{Y}=\mathrm{PL}) ; 8.594 \AA \text { vs. } 0.011(\mathrm{Y}=\mathrm{Cl}) ; 8.883 \AA \text { vs. } \\
& \mathrm{Pt}\left(\mathrm{~K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1}\right)(\mathrm{Y}): 8.891 \AA \text { vs. } 0.023(\mathrm{Y}=\mathrm{Cl}) ; 9.231 \AA \text { i̊ vs. } 0.022(\mathrm{Y}=\mathrm{I}) \\
& \mathrm{Pt}\left(\mathrm{~K}^{3}-\mathrm{P}^{1} \mathrm{~N}^{1} \mathrm{Se}^{1}\right)(\mathrm{Cl}): 9.226 \AA \text { vs. } 0.012
\end{aligned}
$$

Author Contributions: The authors contributed equally. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Science of Slovakia grant number VEGA 1/0514/22, KEGA 027UK-4/2020, and APVV-15-0585.

Acknowledgments: This work was supported by the Comenius University Bratislava, Faculty of Pharmacy, and by projects of the Ministry of Education and Science, Slovakia, VEGA 1/0514/22, KEGA 027UK-4/2020, and APVV-15-0585.

Conflicts of Interest: The authors declare no conflict of interest.

## Abbreviations

$$
\begin{aligned}
& \mathrm{Bu}^{\mathrm{t}} 2^{1} \mathrm{P}^{1}\left(\mathrm{CH}_{2}\right)\left(\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}^{1}\right)\left(\mathrm{CH}_{2}\right) \mathrm{N}^{2} \mathrm{Et}_{2} \\
& \left.\mathrm{Bu}^{\mathrm{t}} \mathrm{~S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SBu}^{\mathrm{t}}\right)\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right) \\
& \mathrm{cyh}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{Si}^{1}\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}\left(\mathrm{Me}_{2}\right)\right) \\
& \mathrm{m} \\
& \mathrm{~N}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{10}\right) \mathrm{NP}^{1}\left(\mathrm{Pr}^{1}\right)\left(\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{N}^{2} \\
& \text { or } \\
& \mathrm{Ph}_{2} \mathrm{P}^{1}\left(\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{CHN}^{1} \mathrm{NCC}^{1} \mathrm{~S}^{1}\right) \cdot \mathrm{NHMe}^{2}\right) \\
& \mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{23} \mathrm{H}_{28} \mathrm{~S}^{1}\right)\left(\mathrm{B}\left(\mathrm{Ph}_{2}\right) \mathrm{Cl}^{1}\right)
\end{aligned}
$$

```
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{4}{}\mp@subsup{\textrm{ClO}}{}{1})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{\textrm{N}}{}{2}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{8}{}\mp@subsup{\textrm{H}}{7}{}\mp@subsup{\textrm{NOO}}{}{1}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{2}{}\mp@subsup{\textrm{H}}{2}{}\textrm{O})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{}OH
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{2}{}\mp@subsup{\textrm{H}}{2}{}\textrm{O})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{}\textrm{OH}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{2}{}\mp@subsup{\textrm{H}}{2}{}\textrm{O})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{6}{}\textrm{OH}
Ph}2\mp@subsup{P}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{3}{}\mp@subsup{\textrm{H}}{6}{})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{O}}{2}{}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{5}{}\mp@subsup{\textrm{H}}{7}{}\textrm{O})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{10}{}\mp@subsup{\textrm{N}}{2}{}
Ph}2\mp@subsup{P}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{})\mp@subsup{\textrm{N}}{}{2}(\mp@subsup{\textrm{C}}{10}{}\mp@subsup{\textrm{H}}{9}{}\mp@subsup{\textrm{NO}}{3}{}
Ph}2\mp@subsup{P}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{\textrm{C}}{}{1})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{\textrm{N}}{}{2}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{MeS}}{}{1})(\mp@subsup{\textrm{Bu}}{}{\textrm{t}}\mp@subsup{\textrm{NH}}{2}{}
Ph}2\mp@subsup{P}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{NC}}{5}{}\mp@subsup{\textrm{H}}{4}{}\mp@subsup{\textrm{N}}{}{2}
Ph}\mp@subsup{\mp@code{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1}\mp@subsup{\textrm{C}}{3}{}\mp@subsup{\textrm{H}}{6}{}\mp@subsup{\textrm{Se}}{}{1}(\textrm{Ph}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{N}}{}{1}\mp@subsup{\textrm{O}}{}{1}
Ph}\mp@subsup{2}{}{P1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{6}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{8}{}\textrm{N})(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{8}{}\mp@subsup{\textrm{N}}{}{2}
Ph}\mp@subsup{2}{2}{}\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{6}{}\mp@subsup{\textrm{N}}{}{1})(\mp@subsup{\textrm{NC}}{7}{}\mp@subsup{\textrm{H}}{5}{}\mp@subsup{\textrm{O}}{}{1})\mp@subsup{\textrm{Ph}}{2}{}\mp@subsup{\textrm{P}}{}{2}(\mp@subsup{\textrm{C}}{15}{}\mp@subsup{\textrm{H}}{13}{}\mp@subsup{\textrm{N}}{2}{}\textrm{O}
Ph}2\mp@subsup{P}{}{1}(\mp@subsup{\textrm{C}}{7}{}\mp@subsup{\textrm{H}}{6}{}\mp@subsup{\textrm{N}}{}{1}=\mp@subsup{\textrm{NCC}}{}{1}\mp@subsup{\textrm{C}}{5}{}\mp@subsup{\textrm{H}}{6}{}
Pr}\mp@subsup{}{}{\textrm{i}}\mp@subsup{\textrm{S}}{}{1}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{})\mp@subsup{\textrm{P}}{}{1}(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{}\mp@subsup{SPPr}{}{\textrm{i}}).(\mp@subsup{\textrm{C}}{6}{}\mp@subsup{\textrm{H}}{4}{})\mp@subsup{\textrm{S}}{}{2}
py
tr
(4-chloro-2-(((2-(diphenylphosphino)phenylimino) methylphenylate
(2-(((2-(diphenylphosphino)phenylimino)methyl-4-methoxyphenylato)
( N -(2-(diphenylphosphinobenzylidene)- N -(2-hydroxyphenyl)glycinamidato)
( \(\mathrm{N}^{2}\)-(2-(diphenylphosphino)benzylidene)- N -(3-hydroxyphenyl)glycinamidato
( N -(2-(diphenylphosphino)benzylidene)-N-(2-hydroxymethylphenyl)glycine-amidato) ( N -(2-((2-(diphenylphosphino)benzylidene)amino) propyl)-2-hydroxybenzamidato)
R7C-(N-(5,7-(dimethyl-1,8-naphtylridin-2-yl)- \(\mathrm{N}^{2}\) -
(2-(diphenylphosphinyl)benzylidene) valinamidato) ( \(\mathrm{N}^{2}\)-benzyloxycarbinol)- N -(2-(((2-(diphenylphosphanyl) phenyl)methylidene) amino)phenyl)glycinamide) (2-(1b)-1-(((2-diphenylphosphinobenzylidene)amine) ethyl)phenyl)
( N -\{N-[2-(diphenylphosphino)benzylidene)]-\}
\{D/L-methionyl\}-terc-butylamine
(2-(2-(diphenylphosphino)benzylidene)-1-(pyridine-2-yl)diazanido
( N -(2-(diphenylphosphino)benzylidene)-N-
(3-(phenylseleno)propyl)amine
(2-diphenylphosphino)-2-aminobenzaldehyde)
( \(\mathrm{N}^{2}\)-(2-(diphenylphosphino)benzyl)- \(\mathrm{N}, \mathrm{N}\)-bis (2-pyridyl-2-ethyl)amine)
\(\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}\right)\left(\mathrm{NC}_{7} \mathrm{H}_{5} \mathrm{O}^{1}\right) \mathrm{Ph}_{2} \mathrm{P}^{2}\left(\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{~N}_{2} \mathrm{O}\right)\)
(N-(2-(diphenylphosphino)-1-phenylformyl)
benzohydiazino)- N -(2-(diphenylphosphino)-1phenylvinyl)benzohydeazone)
\(\mathrm{Ph}_{2} \mathrm{P}^{1}\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{~N}^{1}=\mathrm{NCC}^{1} \mathrm{C}_{5} \mathrm{H}_{6}\right) \quad\) (2-((2-(diphenylphosphino)-4-methylphenyl)diazinyl)\(\left.\operatorname{Pr}^{\mathrm{i}} \mathrm{S}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{P}^{1}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SPr}^{\mathrm{i}}\right) .\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{S}^{2}\right)\) 5-methylphenyl)pyridine (2-(((2-(isopropysulfanyl)phenyl)(2-isopropylsulfanyl) phenyl)phosphino)benzenethiazato) pyridine triclinic
```


## References

1. Holloway, C.E.; Melnik, M. Structural aspect of platinum coordination compounds: Part III—Monomeric square planar (PtA ${ }_{2} \mathrm{XY}$ and PtABXY) and trigonal bipyramidal PtII coordination compounds. Rev. Inorg. Chem. 2004, 24, 135-299. [CrossRef]
2. Holloway, C.E.; Melnik, M. Structural aspect of platinum coordination compounds: Part I-Monomeric Pt0, PtI and PtIIA 4 derivatives. Rev. Inorg. Chem. 2002, 22, 163-284. [CrossRef]
3. Holloway, C.E.; Melnik, M. Structural Aspect of Platinum Coordination Compounds: Part II-Monomeric PtII Compounds with $\mathrm{PtA}_{3} \mathrm{~B}$ and $\mathrm{PtA}_{2} \mathrm{~B}_{2}$ Composition. Rev. Inorg. Chem. 2003, 23, 125-287. [CrossRef]
4. Melnik, M.; Holloway, C.E. Stereochemistry of platinum coordination compounds. Coord. Chem. Rev. 2006, 250, 2261-2270. [CrossRef]
5. Melník, M.; Mikuš, P. Distortion isomers of cis- $\mathrm{PtP}_{2} \mathrm{X}_{2}$ and cis- $\mathrm{PtP}_{2} \mathrm{XY}$ derivatives-Structural aspects. Rev. Inorg. Chem. 2020, 40, 153-165. [CrossRef]
6. Melník, M.; Mikuš, P. Ligand isomerism in Pt(II) complexes—Structural aspects. Rev. Inorg. Chem. 2022, 42, 21-28. [CrossRef]
7. Melník, M.; Mikuš, P. Heterotridentate organodiphosphines in $\operatorname{Pt}\left(\eta^{3}-\mathrm{P}^{1} \mathrm{X}^{1} \mathrm{P}^{2}\right)(\mathrm{Y})\left(\mathrm{X}^{1}=\mathrm{B}, \mathrm{S}\right.$, or Si$)$ and $\mathrm{Pt}\left(\eta^{3}-\mathrm{P}^{1} \mathrm{P}^{2} \mathrm{Si}^{1}\right)(\mathrm{Y})$ derivatives-structural aspects. Rev. Inorg. Chem. 2021, 42, 21-28. [CrossRef]
8. Melník, M.; Mikuš, P. Organodiphosphines in $\operatorname{Pt}\left\{\eta^{2}-\mathrm{P}(\mathrm{X})_{\mathrm{n}} \mathrm{P}\right\} \mathrm{Cl}_{2}(n=9-15,17,18)$ derivatives-Structural aspects. Rev. Inorg. Chem. 2021, 41, 41-48. [CrossRef]
9. Melník, M.; Mikuš, P. Heterotridentate organodiphosphines in $\operatorname{Pt}\left(\eta^{3}-\mathrm{P}^{1} \mathrm{X}^{1} \mathrm{P}^{2}\right)(\mathrm{Y})$ derivatives-structural aspects. Rev. Inorg. Chem. 2021, 41, 41-48. [CrossRef]
10. Vuzman, D.; Poverenov, E.; Shimon, L.J.W.; Diskin-Posner, Y.; Milstein, D. Cationic, Neutral and Anionic Platinum(II) Complexes Based on an Electron-Rich PNN Ligand. New Modes of Reactivity Based on Pincer Hemilability and Dearomatization. Organometallics 2008, 27, 2627-2634. [CrossRef]
11. Durran, S.E.; Elsegood, M.R.J.; Hammond, S.R.; Smith, M.B. Flexible $\kappa^{4}-$ PNN'O-Tetradentate Ligands: Synthesis, Complexation $^{\prime}$ and Structural Studies. Dalton Trans. 2010, 39, 7136-7146. [CrossRef] [PubMed]
12. Durran, S.E.; Elsegood, M.R.J.; Hammond, S.R.; Smith, M.B. Coordination Studies of a New Unsymmetrical $\kappa^{4}-\mathrm{PNN}^{\prime} \mathrm{N}^{\wedge}{ }^{\text {-}}$ Tetradentate Ligand: Stepwise Formation and Structural Characterization. Inorg. Chem. 2007, 46, 2755-2766. [CrossRef] [PubMed]
13. Fuentes, J.A.; Clarke, M.L.; ZSlawin, A.M. A Supramolecular Approach to Chiral Ligand Modification: Coordination Chemistry of a Multifunctionalised Tridentate Amine-Phosphine Ligand. New J. Chem. 2008, 32, 689-693. [CrossRef]
14. Elsegood, M.R.J.; Sanchez-Ballester, N.M.; Smith, M.B. New $\kappa^{3}-\mathrm{PNN}^{\prime}$ - and $\kappa^{4}$-PNN'O-Polydentate Ligands: Synthesis, Coordination and Structural Studies. Inorg. Chim. Acta 2011, 379, 115-121. [CrossRef]
15. Chang, M.; Horiki, H.; Nakajima, K.; Kobayashi, A.; Chang, H.-C.; Kato, M. Acid-Base Behavior of Substituted Hydrazone Complexes Controlled by the Coordination Geometry. Bull. Chem. Soc. Jpn. 2010, 83, 905-910. [CrossRef]
16. Watkins, S.E.; Craig, D.C.; Colbran, S.B. Towards Co-Operative Reactivity in Conjoint Classical-Organometallic Heterometallic Complexes: The Co-Ordination Chemistry of Novel Ligands with Triphenylphosphine and Bis(Pyridylethyl)Amine or Triazacyclononane Domains. J. Chem. Soc. Dalton Trans. 2002, 12, 2423-2436. [CrossRef]
17. Ahmad, M.; Perera, S.D.; Shaw, B.L.; Thornton-Pett, M. Uni-, Bi- and Ter-Dentate Complexes Formed from $\mathrm{PPh}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{R}) \mathrm{NNHC}(\mathrm{O}) \mathrm{Ph}$ ( $\mathrm{R}=\mathrm{But}$ or Ph ) and Pd or Pt: Crystal Structures of $\left[\mathrm{PdCl}\left\{\mathrm{PPh}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{But}) \mathrm{NNC}(\mathrm{Ph}) \mathrm{O}\right\}\right],\left[\mathrm{Pt}\left\{\mathrm{PPh}_{2} \mathrm{CHC}(\mathrm{Ph}) \mathrm{NNC}(\mathrm{Ph}) \mathrm{O}^{2}\left\{\mathrm{PPh}_{2} \mathrm{CH}_{2} \mathrm{C}(\mathrm{Ph})\right.\right.\right.$ NNHC(O)Ph\}] and [ $\mathrm{Pd}\left\{\mathrm{PPh}_{2} \mathrm{CHC}(\mathrm{But}) \mathrm{NHNC}(\mathrm{O}) \mathrm{Ph}\right\}_{2}$ ]. J. Chem. Soc. Dalton Trans. 2002, 9, 1954-1962. [CrossRef]
18. Ní Dhubhghaill, O.M.; Lennon, J.; Drew, M.G.B. Palladium(Ii) and Platinum(Ii) Complexes with Tridentate Iminophosphine Ligands; Synthesis and Structural Studies. Dalton Trans. 2005, 19, 3213-3220. [CrossRef]
19. Jircitano, A.J.; Mertes, K.B. Ligands with Dual Denticity: Crystal and Molecular Structure of Dichloro-Bis(o-Diphenylphosphino)Benzaldehyde)Platinum(II). Inorg. Chim. Acta 1985, 103, L11-L13. [CrossRef]
20. Kano, N.; Yamamura, M.; Meng, X.; Yasuzuka, T.; Kawashima, T. Different Coordination Modes of 2-(Diphenylphosphino)Azobenzenes in Complexation with Hard and Soft Metals. Dalton Trans. 2012, 41, 11491-11496. [CrossRef]
21. Ramírez, P.; Contreras, R.; Valderrama, M.; Carmona, D.; Lahoz, F.J.; Balana, A.I. Cyclometallated Platinum(II) Complexes Containing the Chiral Ligand [2-(Diphenyl-Phosphanyl)-Benzylidene]-(1-Phenyl-Ethyl)-Amine: Synthesis and Molecular Structures of the Compounds $\left[\mathrm{PtCl}(\mathrm{Me})\left\{\mathrm{K}^{2}-(\mathrm{R})-\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{CHNCH}(\mathrm{Ph}) \mathrm{Me}-\mathrm{P}, \mathrm{N}\right\}\right]$ and $\left[\mathrm{Pt}\left\{\mathrm{K}^{3}-(\mathrm{S})-\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right) \mathrm{CHN}\right.\right.$. J. Organomet. Chem. 2008, 693, 349-356. [CrossRef]
22. You, D.; Kang, S.O.; Ko, J.J.; Choi, M. Cycloplatinated complexes of thiosemicarbazones. Synthesis and crystal structure of [ $\left.\mathrm{Ph}_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{CHNNC}(\mathrm{S}) \mathrm{NHCH}_{3} \mathrm{PtCl}\right]$. Bull. Korean Chem. Soc. 1997, 18, 305-310.
23. Ankersmit, H.A.; Veldman, N.; Spek, A.L.; Vrieze, K.; van Koten, G. Methyl-, Acetyl- and Allyl-Palladium and -Platinum Complexes Containing Novel Terdentate PNS and NN'S Ligands. Inorg. Chim. Acta 1996, 252, 339-354. [CrossRef]
24. Durran, S.E.; Elsegood, M.R.J.; Smith, M.B. New Complexes of Functionalised Ligands Bearing P/N/Se or P $\mathrm{P}_{2}$ Se Donor Sets. New J. Chem. 2002, 26, 1402-1408. [CrossRef]
25. Edwards, P.G.; Kariuki, B.; Newman, P.D. Coordination Behaviour in Transition Metal Complexes of Asymmetric NPN Ligands. Polyhedron 2011, 30, 935-941. [CrossRef]
26. Takeda, N.; Tanaka, Y.; Oma, R.; Sakakibara, F.; Unno, M. Activation of C-S Bond by Group 10 Metal Complexes: Reaction of Phosphine Ligand Tethered with Three tert-Butylthiophenyl Groups with Group 10 Metal Compounds. Bull. Chem. Soc. Jpn. 2016, 89, 922-930. [CrossRef]
27. Emslie, D.J.H.; Cowie, B.E.; Oakley, S.R.; Huk, N.L.; Jenkins, H.A.; Harrington, L.E.; Britten, J.F. A Study of M-X-BR3 ( $\mathrm{M}=\mathrm{Pt}$, Pd or Rh; $\mathrm{X}=\mathrm{Cl}$ or I) Interactions in Square Planar Ambiphilic Ligand Complexes: Structural, Spectroscopic, Electrochemical and Computational Comparisons with Borane-Free Analogues. Dalton Trans. 2012, 41, 3523-3535. [CrossRef] [PubMed]
28. Takaya, J.; Ito, S.; Nomoto, H.; Saito, N.; Kirai, N.; Iwasawa, N. Fluorine-Controlled C-H Borylation of Arenes Catalyzed by a PSiN-Pincer Platinum Complex. Chem. Commun. 2015, 51, 17662-17665. [CrossRef]
29. Yang, L.; Powell, D.R.; Houser, R.P. Structural Variation in Copper(i) Complexes with Pyridylmethylamide Ligands: Structural Analysis with a New Four-Coordinate Geometry Index, $\tau_{4}$. Dalton Trans. 2007, 9, 955-964. [CrossRef]
