# Variable Combinations of Tridentate Ligands in $\operatorname{Pt}\left(\eta^{3}-\right.$ $\left.X_{3} \mathrm{~L}\right)(\mathrm{PL})$ Derivatives 

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There are over fifty examples in which the inner coordination spheres about the $\mathrm{Pt}(\mathrm{II})$ atoms of the $\mathrm{Pt}\left(\eta^{3}-\mathrm{X}_{3} \mathrm{~L}\right)(\mathrm{PL})$ type are formed by variable combinations of donor atoms of tridentate ligands. Each $\eta^{3}$-ligand creates two metallocyclic rings. The complexes based on membered metallocyclic rings can be divided into four groups: 1. 6+6-Membered Metallocyclic Rings, 2. 6+5-Membered Metallocyclic Rings, 3. 5+6-Membered Metallocyclic Rings, and 4. 5+5-Membered Metallocyclic Rings.

Keywords: structure ; Pt(n3-X3L)(PL) ; distortion ; trans-effect

## 1. 6+6-Membered Metallocyclic Rings

There are only three examples in which a $\eta^{3}$-ligand creates such rings (Table 1). In [ $\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{22} \mathrm{H}_{11} \mathrm{~F}_{6} \mathrm{~N}_{3} \mathrm{O}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)$ $\left.\left(\mathrm{PPh}_{3}\right)\right]$ (at 173 K ) ${ }^{[1]}$, the $\eta^{3}$-ligand forms a metallocyclic ring of the $\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{2}$ type with common ligating $\mathrm{N}^{1}$ atoms. The values of the chelate L-Pt-L angles are $90.6^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $90.2^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{2}\right)$. The $\mathrm{O}^{1} \mathrm{C}_{2} \mathrm{NN}^{1} \mathrm{C}_{3} \mathrm{O}^{2}$ type with the respective chelate angles of $88.2^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $90.0^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{2}\right)$ was found in $\left[\mathrm{Pt}\left(\mathrm{n}^{3}-\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{3}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)\left(\mathrm{PPR}_{3}\right)\right]$ (at $150 \mathrm{~K})^{[2]}$. The remaining L-Pt-L angles open in the following order (mean values): 88.1 ${ }^{\circ}\left(\mathrm{O}^{2}-\mathrm{Pt}-\mathrm{P}\right)<89.0^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{P}\right)<$ $176.0^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{P}\right)<177.7^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{O}^{2}\right)$. The monodentate $\mathrm{PPh}_{3}$ displayed square-planar geometry about each $\mathrm{Pt}(\mathrm{II})$ atom. The Pt-L bond distance increased in the following order (mean values): $1.995 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$ trans to $\mathrm{O}^{2}$ ) $<1.996 \AA\left(\mathrm{Pt}-\mathrm{O}^{2}\right)<$ $2.010 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right)<2.254 \AA(\mathrm{Pt}-\mathrm{P})$.

Table 1. Structural data for $\operatorname{Pt}\left(\eta^{3}-\mathrm{X}_{3}\right)(\mathrm{Y})$ derivatives. ${ }^{\text {a }}-6+6$-membered metallocyclic rings.

| Complex | Chromophore Chelate Rings $\mathrm{T}_{4}{ }^{\text {b }}$ | $\begin{aligned} & \text { Pt -L }{ }^{c} \\ & (\AA) \text {. } \end{aligned}$ | $\begin{aligned} & \text { L-Pt-L }{ }^{c} \\ & \left({ }^{\circ}\right) \end{aligned}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} {\left[\mathrm{Pt}\left(\mathrm{~h}^{3}-\mathrm{C}_{22} \mathrm{H}_{11} \mathrm{~F}_{6} \mathrm{~N}_{3} \mathrm{O}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right]} \\ (\text { at } 173 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{O}^{2} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{2}\right) \\ 0.032 \end{gathered}$ |  | $\mathrm{O}^{1}, \mathrm{~N}^{1} 90.6{ }^{\text {d }}$ | [1] |
|  |  | $\mathrm{O}^{11.994(2)}$ | $\mathrm{N}^{1}, \mathrm{O}^{2} 90.2{ }^{\text {d }}$ |  |
|  |  | $\mathrm{N}^{1}$ 2.021(2) | $\mathrm{O}^{1}, \mathrm{O}^{2} 179.0$ |  |
|  |  | $\mathrm{O}^{2} 2.004(2)$ | $0^{1}, \mathrm{P} 90.6$ |  |
|  |  | P 2.256 (2) | $\mathrm{O}^{2}$, P 87.5 |  |
|  |  |  | $\mathrm{N}^{1}, \mathrm{P} 177.0$ |  |
| $\begin{gathered} {\left[\mathrm{Pt}\left(\mathrm{\eta}^{3}-\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{3}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right]} \\ (\text { at } 150 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{O}^{2} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{2} \mathrm{NN}^{1} \mathrm{C}_{3} \mathrm{O}^{2}\right) \\ 0.024 \end{gathered}$ |  | $\mathrm{O}^{1}, \mathrm{~N}^{1} 88.2{ }^{\text {d }}$ | [2] |
|  |  | $\mathrm{O}^{11.995(2)}$ | $\mathrm{N}^{1}, \mathrm{O}^{2} 90.0{ }^{\text {d }}$ |  |
|  |  | $\mathrm{N}^{1} 2.000$ (2) | $\mathrm{O}^{1}, \mathrm{O}^{2} 176.5$ |  |
|  |  | $\mathrm{O}^{2} 1.988$ (2) | $\mathrm{O}^{1, \mathrm{P}} 89.0$ |  |
|  |  | P 2.251(2) | $\mathrm{O}^{2}, \mathrm{P} 90.7$ |  |
|  |  |  | $\mathrm{N}^{1}$, P 175.0 |  |
| $\left[\mathrm{Pt}\left\{\mathrm{n}^{3}-\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{~S}_{3}-\mathrm{S}^{\mathbf{1}}, \mathrm{S}^{\mathbf{2}}, \mathrm{S}^{\mathbf{3}}\right\}\left(\mathrm{PPh}_{3}\right)\right] \mathrm{BF}_{4}$ | $\begin{gathered} \operatorname{PtS}^{1} \mathrm{~S}^{2} \mathrm{~S}^{3} \mathrm{P}\left(\mathrm{~S}^{1} \mathrm{C}_{3} \mathrm{~S}^{2} \mathrm{C}_{3} \mathrm{~S}^{3}\right) \\ 0.035 \end{gathered}$ |  | $S^{1}, S^{2} 87.1(2){ }^{\text {d }}$ | [3] |
|  |  | $\mathrm{S}^{1} 2.330(2)$ | $\mathrm{S}^{2}, \mathrm{~S}^{3} 89.5(2){ }^{\text {d }}$ |  |
|  |  | $\mathrm{S}^{2}$ 2.339(2) | $\mathrm{S}^{1}, \mathrm{~S}^{3} 176.3(2)$ |  |
|  |  | $\mathrm{S}^{3} 2.336(2)$ | $\mathrm{S}^{1, \mathrm{P}} 91.1(2)$ |  |
|  |  | P 2.332(2) | $\mathrm{S}^{3}, \mathrm{P} 92.3(1)$ |  |
|  |  |  | $\mathrm{S}^{2}, \mathrm{P}$ 171.0(2) |  |

${ }^{( }{ }^{\text {a }}$ ) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. $\left({ }^{(b}\right)$ Parameter $\tau_{4}$, degree of distortion. $\left({ }^{c}\right)$ The chemical identity of the coordinated atom/ligand is specific to these columns. $\left({ }^{d}\right)$ Six-membered metallocyclic ring.

For the complex $\left[\operatorname{Pt}\left\{\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{~S}_{3}-\mathrm{S}^{1}, \mathrm{~S}^{2}, \mathrm{~S}^{3}\right\}\left(\mathrm{PPh}_{3}\right)\right] \mathrm{BF}_{4}$, the $\eta^{3}$-ligand creates a pair of six-membered metallocyclic rings of the $\mathrm{S}^{1} \mathrm{C}_{3} \mathrm{~S}^{2} \mathrm{C}_{3} \mathrm{~S}^{3}$ type (as shown in Figure 1) ${ }^{[3]}$. The values of the chelate angles are $87.1^{\circ}\left(\mathrm{S}^{1}\right.$-Pt- $\left.\mathrm{S}^{2}\right)$ and $89.5^{\circ}\left(\mathrm{S}^{2}\right.$-Pt-
$\mathrm{S}^{3}$ ). The remaining L-Pt-L bond angles open in the following order: $91.1^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{P}\right)<92.3^{\circ}\left(\mathrm{S}^{3}-\mathrm{Pt}-\mathrm{P}\right)<171.0^{\circ}\left(\mathrm{S}^{2}-\mathrm{Pt}-\mathrm{P}\right)<$ $176.3^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{S}^{3}\right)$. The Pt-L bond distance increases in the following order: $2.330 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<2.332 \AA(\mathrm{Pt}-\mathrm{P})<2.336 \AA$ (Pt$\mathrm{S}^{3}$ ) $<2.339 \AA$ (Pt- $\mathrm{S}^{2}$ trans to P ). Noticeably, the trans $-\mathrm{X}^{1}-\mathrm{Pt}-\mathrm{X}^{3}$ bond angles are somewhat bigger than the trans- $\mathrm{X}^{2}-\mathrm{Pt}-\mathrm{P}$ bond angles (Table 1).


Figure 1. Structure of $\left[\mathrm{Pt}\left\{\mathrm{\eta}^{3}-\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{~S}_{3}-\mathrm{S}^{1}, \mathrm{~S}^{2}, \mathrm{~S}^{3}\right\}\left(\mathrm{PPh}_{3}\right)\right]{ }^{[3]}$.

## 2. 6+5-Membered Metallocyclic Rings

There are five examples namely $\left[\mathrm{Pt}\left(\mathrm{\eta}^{3}-\mathrm{C}_{16} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{OS}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]{ }^{4]}$, $\left[\mathrm{Pt}\left(\mathrm{\eta}^{3}-\mathrm{C}_{16} \mathrm{H}_{13} \mathrm{~N}_{3} \mathrm{O}_{3} \mathrm{~S}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]$ (at 200K) ${ }^{[4]},\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{8} \mathrm{H}_{8} \mathrm{~N}_{3} \mathrm{OS}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]$ toluene ${ }^{[5]}$, $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{9} \mathrm{H}_{9} \mathrm{~N}_{3} \mathrm{OS}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]$ (at 100 K ) (Figure 2) [6], and $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{OS}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]{ }^{[4]}$ (Table 2). In each of them, the $\eta^{3}$-ligand creates six- and five-membered metallocyclic rings with a common ligating $N^{1}$ atom of the $\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}$ type. The values of the respective chelate angles (mean values) are $92.3^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right)$ and $84.6^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. The remaining L-Pt-L bond angles open in the following order (mean values): $90.7^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{P}\right)<92.4^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{P}\right)<175.8^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{P}\right)<175.9^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{S}^{1}\right)$. Interestingly, the mean values of both trans- $\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{S}^{1}$ and $\mathrm{N}^{1}$-Pt-P angles are equal. The Pt-L bond distance increases (mean values) in the following order: $2.028 \AA\left(\mathrm{Pt}-\mathrm{O}^{1}\right.$ trans to $\left.\mathrm{S}^{1}\right)<2.035 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right.$ trans to P$)<2.244 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<2.259 \AA(\mathrm{Pt}-\mathrm{P})$.


Figure 2. Structure of $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{9} \mathrm{H}_{9} \mathrm{~N}_{3} \mathrm{OS}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{~S}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]^{[6]}$.
Table 2. Structural data for $\operatorname{Pt}\left(\eta^{3}-X_{3}\right)(Y)$ derivatives. ${ }^{\text {a }}-6+5-$ membered metallocyclic rings.

## Complex

Chromophore Chelate Rings $\mathrm{T}_{4}{ }^{\text {b }}$
(A)
$\mathrm{O}^{1} 1.992$
$\mathrm{~N}^{1} 2.034$
$\mathrm{~S}^{1} 2.245$
P 2.258
$0^{1} 2.001$
$\mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}\right)$ 0.018

## $\mathrm{O}^{1} 1.992$ <br> $\mathrm{N}^{1} 2.034$ P 2.258

$\mathrm{N}^{1} 2.041$ $\mathrm{S}^{1} 2.239$

Pt -L P 2.248
$0^{1} 2.015$
$\mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}\right)$
0.020
$\mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}\right)$
0.024

L-Pt-L ${ }^{\text {c }}$
( ${ }^{\circ}$ )
$\mathrm{O}^{1}, \mathrm{~N}^{1} 91.2^{\mathrm{d}}$
$\mathrm{N}^{1}, \mathrm{~S}^{1} 85.0^{\mathrm{e}}$
$\mathrm{O}^{1}, \mathrm{~S}^{1} 176.0$ $\mathbf{O}^{1}$, P 89.0 $\mathrm{S}^{1}$, P 93.1 $\mathrm{N}^{1}$, P 178.1
$\mathrm{O}^{1}, \mathrm{~N}^{1} 92.6^{\mathrm{d}}$
$\mathrm{N}^{1}, \mathbf{S}^{1} 85.3^{\mathrm{e}}$ $\mathrm{O}^{1}, \mathrm{~S}^{1} 177.6$ $\mathrm{O}^{1}, \mathrm{P} 89.0$ $\mathrm{S}^{1}, \mathrm{P} 93.3$ $\mathrm{N}^{1}$, P 176.0
$\mathrm{O}^{1}, \mathrm{~N}^{1} 93.1^{\mathrm{d}}$ $\mathrm{N}^{1}, \mathrm{~S}^{1} 83.8^{\mathrm{e}}$ $\mathrm{O}^{1}, \mathrm{~S}^{1} 176.6$ $\mathrm{O}^{1}, \mathrm{P} 89.9$ $\mathrm{S}^{1}, \mathrm{P} 93.3$ $\mathrm{N}^{1}$, P 176.3
$\mathrm{O}^{1}, \mathrm{~N}^{1} 92.5^{\mathrm{d}}$ $\mathrm{N}^{1}, \mathrm{~S}^{1} 85.1^{\mathrm{e}}$ $\mathrm{O}^{1}, \mathbf{S}^{1} 175.7$ $\mathrm{O}^{1}, \mathrm{P} 91.5$ $\mathbf{S}^{1}$, P 91.0 $\mathrm{N}^{1}, \mathrm{P} 175.6$

Ref.

Pt - ${ }^{\text {c }}$
(A)

|  | $O^{1}, N^{1} 92.3^{\mathrm{d}}$ |  |
| :---: | :---: | :---: |
| $\mathrm{PtO}^{1} \mathrm{~N}^{1} \mathrm{~S}^{1} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{3} \mathrm{~N}^{1} \mathrm{NCS}^{1}\right)$ | $\mathrm{O}^{1} 2.045$ | $\mathrm{~N}^{1}, \mathrm{~S}^{1} 83.2^{\mathrm{e}}$ |
| 0.037 | $\mathrm{~N}^{1} 2.029$ | $\mathrm{O}^{1}, \mathrm{~S}^{1} 173.6$ |
|  | $\mathrm{~S}^{1} 2.246$ | $\mathrm{O}^{1}, \mathrm{P} 93.1$ |
|  | P 2.269 | $\mathrm{~S}^{1}, \mathrm{P} 91.2$ |
|  |  | $\mathrm{~N}^{1}, \mathrm{P} 173.1$ |

L-Pt-L ${ }^{c}$

Ref.
( ${ }^{\circ}$ )

$\mathrm{O}^{1}, \mathrm{~N}^{1} 92.3^{\mathrm{d}}$
, $\mathrm{O}^{1}, \mathrm{P} 93.1$ $\mathbf{N}^{1}$, P 173.1
$\left.{ }^{( }{ }^{a}\right)$ Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. $\left({ }^{(b}\right)$ Parameter $\tau_{4}$, degree of distortion. $\left({ }^{c}\right)$ The chemical identity of the coordinated atom/ligand is specific to these columns. ( $\left.{ }^{( }\right)$Six-membered metallocyclic ring. $\left({ }^{( }\right)$Five-membered metallocyclic ring.

## 3. 5+6-Membered Metallocyclic Rings

There are four complexes mentioned in this section, namely $\left[\operatorname{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{~N}_{4}-\mathrm{N}^{1}, \mathrm{~N}^{2}, \mathrm{~N}^{3}\right)\left(\mathrm{PPh}_{3}\right)\right]$ (at 100 K$){ }^{[7]},\left[\mathrm{Pt}\left(\eta^{3}-\right.\right.$ $\left.\left.\left.\mathrm{C}_{13} \mathrm{H}_{9} \mathrm{NO}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right]\right]_{8}^{[8]},\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Se}_{2}-\mathrm{Se}^{1}, \mathrm{~N}^{1}, \mathrm{Se}^{2}\right)\left\{\mathrm{P}\left(\eta^{1}-\mathrm{C}_{11} \mathrm{H}_{19} \mathrm{O}_{5}\right)(\mathrm{Ph})_{2}\right\}\right]{ }^{[9]}$, and $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{29} \mathrm{H}_{20} \mathrm{~F}_{6} \mathrm{~S}_{2} \mathrm{O}-\right.\right.$ $\left.\left.\mathrm{S}^{1}, \mathrm{~S}^{2}, \mathrm{O}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]$ (at 100 K ) ${ }^{[10]}$, and their structural parameters are gathered in Table 3. The structure of $\left[\mathrm{Pt}\left(\mathrm{n}^{3}-\right.\right.$ $\left.\left.\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{~N}_{4}-\mathrm{N}^{1}, \mathrm{~N}^{2}, \mathrm{~N}^{3}\right)\left(\mathrm{PPh}_{3}\right)\right][7]$ is shown in Figure 3 as an example. Each $\eta^{3}$-ligand creates five and six metallocyclic rings. The donor atoms of the respective $\eta^{3}$-ligands play a role in the size of the L-Pt-L chelate angles. These angles increase in the following sequences:


Figure 3. Structure of $\left[\operatorname{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{~N}_{4}-\mathrm{N}^{1}, \mathrm{~N}^{2}, \mathrm{~N}^{3}\right)\left(\mathrm{PPh}_{3}\right)\right]{ }^{[7]}$.
Table 3. Structural data for $\operatorname{Pt}\left(\eta^{3}-X_{3}\right)(Y)$ derivatives. ${ }^{\text {a }}-5+6$-membered metallocyclic rings.

| Complex | Chromophore Chelate Rings $\mathrm{t}_{4}{ }^{\text {b }}$ | $\text { Pt }-L^{c}$ <br> (A) | $\begin{aligned} & \text { L-Pt-L }{ }^{\mathrm{c}} \\ & \left({ }^{\circ}\right) \end{aligned}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} {\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{~N}_{4}-\mathrm{N}^{1}, \mathrm{~N}^{2}, \mathrm{~N}^{3}\right)\left(\mathrm{PPh}_{3}\right)\right]} \\ (\mathrm{at} 100 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \text { Pt } \mathrm{N}^{1} \mathrm{~N}^{2} \mathrm{~N}^{3} \mathrm{P}\left(\mathrm{~N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} \mathrm{NC}_{2} \mathrm{~N}^{3}\right) \\ 0.034 \end{gathered}$ | $\begin{aligned} & \mathrm{N}^{1} 1.984 \\ & \mathrm{~N}^{2} 2.025 \\ & \mathrm{~N}^{3} 1.964 \\ & \mathrm{P} 2.255 \end{aligned}$ | $\mathrm{N}^{1}, \mathrm{~N}^{2} 81.7^{\mathrm{e}}$ <br> $\mathrm{N}^{2}, \mathrm{~N}^{3} 89.6{ }^{\mathrm{d}}$ <br> $\mathrm{N}^{1}, \mathrm{~N}^{3} 170.6$ <br> $\mathrm{N}^{1}, \mathrm{P} 93.0$ <br> $\mathrm{N}^{3}, \mathrm{P} 96.3$ <br> $\mathrm{N}^{2}$, P 177.2 | [7] |
| $\left[\mathrm{Pt}\left(\mathrm{n}^{3}-\mathrm{C}_{13} \mathrm{H}_{9} \mathrm{NO}_{2}-\mathrm{O}^{1}, \mathrm{~N}^{1}, \mathrm{O}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right]$ | $\begin{gathered} \text { Pt } \mathrm{O}^{1} \mathrm{~N}^{1} \mathrm{O}^{2} \mathrm{P}\left(\mathrm{O}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{2}\right) \\ 0.034 \end{gathered}$ | $\begin{gathered} \mathrm{O}^{1} 1.975(9) \\ \mathrm{N}^{1} \\ 2.064(12) \\ \mathrm{O}^{2} 1.996(9) \\ \mathrm{P} 2.248 \end{gathered}$ | $\begin{gathered} \mathrm{O}^{1}, \mathrm{~N}^{1} 82.4(4) \mathrm{e} \\ \mathrm{~N}^{1}, \mathrm{O}^{2} 94.8(4) \\ { }_{\mathrm{d}} \\ \mathrm{O}^{1}, \mathrm{O}^{2} 176.4(4) \\ \mathrm{O}^{1}, \mathrm{P} 91.5(3) \\ \mathrm{O}^{2}, \mathrm{P} 91.5(3) \\ \mathrm{N}^{1}, \mathrm{P} 172.4 \end{gathered}$ | [8] |
| $\begin{gathered} {\left[\mathrm { Pt } ( \eta ^ { 3 } - \mathrm { C } _ { 1 2 } \mathrm { H } _ { 1 6 } \mathrm { N } _ { 2 } \mathrm { O } _ { 4 } \mathrm { Se } _ { 2 } - \mathrm { Se } ^ { 1 } , \mathrm { N } ^ { 1 } , \mathrm { Se } ^ { 2 } ) \left\{\mathrm{P}\left(\boldsymbol{\eta}^{1}-\mathrm{C}_{11} \mathrm{H}_{19} \mathrm{O}_{5}\right)\right.\right.} \\ \left.\left.(\mathrm{Ph})_{2}\right\}\right] \end{gathered}$ | $\begin{gathered} \mathrm{Pt} \mathrm{Se}{ }^{1} \mathrm{~N}^{1} \mathrm{Se}^{2} \\ \left(\mathrm{Se}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{NC}_{2} \mathrm{Se}^{2}\right) \\ 0.036 \end{gathered}$ | $\begin{gathered} \mathrm{Se}^{1} 2.394 \\ \mathrm{~N}^{1} 2.078 \\ \mathrm{Se}^{2} 2.349 \\ \mathrm{P} 2.259 \end{gathered}$ | $\begin{gathered} \mathrm{Se}^{1}, \mathrm{~N}^{1} 83.3^{\mathrm{e}} \\ \mathrm{~N}^{1}, \mathrm{Se}^{2} 98.3^{\mathrm{d}} \\ \mathrm{Se}^{1}, \mathrm{Se}^{3} 176.3 \\ \mathrm{Se}^{1}, \mathrm{P} 87.2 \\ \mathrm{Se}^{2}, \mathrm{P} 90.7 \\ \mathrm{~N}^{1}, \mathrm{P} 170.9 \end{gathered}$ | [9] |
| $\begin{gathered} {\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{29} \mathrm{H}_{20} \mathrm{~F}_{6} \mathrm{O}_{4} \mathrm{~S}_{2} \mathrm{O}-\mathrm{S}^{1}, \mathrm{~S}^{2}, \mathrm{O}^{1}\right)\left(\mathrm{PPh}_{3}\right)\right]} \\ (\text { at } 100 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \text { Pt S } \mathrm{S}^{1} \mathrm{~S}^{2} \mathrm{O}^{1} \mathrm{P}\left(\mathrm{~S}^{1} \mathrm{C}_{2} \mathrm{~S}^{2} \mathrm{C}_{3} \mathrm{O}^{1}\right) \\ 0.059 \end{gathered}$ | $\begin{aligned} & \mathbf{S}^{1} 2.268 \\ & \mathbf{S}^{2} 2.277 \\ & \mathrm{O}^{1} 2.066 \\ & \mathrm{P} 2.253 \end{aligned}$ | $\begin{gathered} \mathbf{S}^{1}, \mathrm{~S}^{2} 90.2^{\mathrm{e}} \\ \mathbf{S}^{1}, \mathrm{O}^{1} 99.2^{\mathrm{d}} \\ \mathrm{~S}^{1}, \mathrm{O}^{1} 169.6 \\ \mathrm{~S}^{1}, \mathrm{P} 89.2 \\ \mathrm{O}^{1}, \mathrm{P} 99.2 \\ \mathbf{S}^{2} \mathrm{P} 169.4 \end{gathered}$ | [10] |

$\left.{ }^{( }{ }^{2}\right)$ Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. $\left(^{( }\right)$Parameter $\tau_{4}$, degree of distortion. $\left(^{c}\right)$ The chemical identity of the coordinated atom/ligand is specific to these columns. $\left({ }^{\text {d }}\right)$ Six-membered metallocyclic ring. $\left({ }^{( }\right)$Five-membered metallocyclic ring.

$$
\begin{gathered}
\mathrm{N}^{1} \mathrm{C}_{2} \mathrm{~N}^{2} \mathrm{NC}_{2} \mathrm{~N}^{3}-81.7^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{N}^{2}\right) \text { and } 89.6^{\circ}\left(\mathrm{N}^{2}-\mathrm{Pt}-\mathrm{N}^{3}\right) ; \\
\mathrm{O}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{C}_{3} \mathrm{O}^{2}-2.4^{\circ}\left(\mathrm{O}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right) \text { and } 94.8^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{O}^{2}\right) ; \\
\mathrm{Se}^{1} \mathrm{C}_{2} \mathrm{~N}^{1} \mathrm{NC}_{2} \mathrm{Se}^{2}-83.3^{\circ}\left(\mathrm{Se}^{1}-\mathrm{Pt}-\mathrm{N}^{1}\right) \text { and } 98.3^{\circ}\left(\mathrm{N}^{1}-\mathrm{Pt}-\mathrm{Se}^{2}\right) ; \\
\mathrm{S}^{1} \mathrm{C}_{2} \mathrm{~S}^{2} \mathrm{C}_{3} \mathrm{O}^{1}-90.2^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right) \text { and } 99.2^{\circ}\left(\mathrm{S}^{2}-\mathrm{Pt}-\mathrm{O}^{1}\right) .
\end{gathered}
$$

The monodentate PL displayed distorted square-planar geometry about $\mathrm{Pt}(\mathrm{II})$ atoms. The $\mathrm{Pt}-\mathrm{L}$ bond distance to PL increased in the following order: $2.025 \AA\left(\mathrm{Pt}-\mathrm{N}^{2}\right)<2.064 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right)<2.078 \AA\left(\mathrm{Pt}-\mathrm{N}^{1}\right)<2.277 \AA\left(\mathrm{Pt}-\mathrm{S}^{2}\right)$. The order follows the above-mentioned sentence for the Pt - L ( L is a common central ligating atom between five and six-rings).

## 4. 5+5-Membered Metallocyclic Rings

There are thirty-nine compounds in which each $\eta^{3}$-ligand creates two five-membered metallocyclic rings. These complexes based on variable combinations of atoms involved in the chelate angles can be divided into twelve groups.

The structure of $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{33} \mathrm{H}_{24} \mathrm{P}_{2} \mathrm{~S}_{2}-\mathrm{S}^{1}, \mathrm{C}^{1}, \mathrm{~S}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right] . \mathrm{CH}_{2} \mathrm{Cl}_{2}{ }^{[11]}$ is shown in Figure 4. The $\eta^{3}$-ligand creates two fivemembered metallocyclic rings with a common $\mathrm{C}^{1}$ atom of the $\mathrm{S}^{1} \mathrm{PCC}^{1} \mathrm{CPS}^{2}$ type with chelate angles of $87.9^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{C}^{1}\right)$ and $87.7^{\circ}\left(\mathrm{C}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)$. This is the only example of this type. The $\mathrm{PPh}_{3}$ demonstrated distorted square-planar geometry about $\mathrm{Pt}(\mathrm{II})$ atoms. The remaining L-Pt-L bond angles open in the following order: $89.7^{\circ}$ ( $\mathrm{S}^{1}$ - Pt-P) < $94.2^{\circ}\left(\mathrm{S}^{2}-\mathrm{Pt}-\mathrm{P}\right)<$ $173.8^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)<176.9^{\circ}\left(\mathrm{C}^{1}-\mathrm{Pt}-\mathrm{P}\right)$. The Pt-L bond distance increases in the following order: $2.020 \AA\left(\mathrm{Pt}-\mathrm{C}^{1}\right)<2.316 \AA$ $\left(\mathrm{Pt}-\mathrm{S}^{2}\right)<2.332 \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<2.322 \AA(\mathrm{Pt}-\mathrm{P})$.


Figure 4. Structure of $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{33} \mathrm{H}_{24} \mathrm{P}_{2} \mathrm{~S}_{2}-\mathrm{S}^{1}, \mathrm{C}^{1}, \mathrm{~S}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right]{ }^{[11]}$.
In another two complexes, namely $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{Te}_{3}-\mathrm{Te}^{1}, \mathrm{Te}^{2}, \mathrm{Te}^{3}\right)\left(\mathrm{PPh}_{3}\right)\right] . \mathrm{C}_{6} \mathrm{H}_{6}$ and $\left[\mathrm{Pt}\left(\eta^{3}-\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{2} \mathrm{Te}_{3}-\mathrm{Te}^{1}, \mathrm{Te}^{2}, \mathrm{Te}^{3}\right)\right.$ $\left.\left(\mathrm{PPh}_{3}\right)\right]{ }^{[12]}$, which are isostructural, the $\eta^{3}$-ligand creates a pair of five-membered metallocyclic rings with common central ligating $\mathrm{Te}^{2}$ atoms of the $\mathrm{Te}^{1} \mathrm{CNTe}^{2} \mathrm{NCTe}^{3}$ type. The mean values of the respective angles are $92.2( \pm 6)^{\circ}\left(\mathrm{Te}^{1}-\mathrm{Pt}-\mathrm{Te}^{2}\right)$ and $92.0( \pm 6)^{\circ}\left(\mathrm{Te}^{2}-\mathrm{Pt}-\mathrm{Te}^{3}\right)$. The $\mathrm{PPh}_{3}$ ligand demonstrated distorted square-planar geometry about each $\mathrm{Pt}(\mathrm{II})$ atom. The remaining L-Pt-L bond angles open in the following order (mean values): $88.1( \pm 1.2)^{\circ}\left(\mathrm{Te}^{3}-\mathrm{Pt}-\mathrm{P}\right) \sim 88.1( \pm 2.31)^{\circ}\left(\mathrm{Te}^{1}-\mathrm{Pt}-\mathrm{P}\right)$ $<173.3( \pm 8)^{\circ}\left(\mathrm{Te}^{1}-\mathrm{Pt}-\mathrm{Te}{ }^{3}\right)<173.4( \pm 2.1)^{\circ}\left(\mathrm{Te}^{2}-\mathrm{Pt}-\mathrm{P}\right)$. The Pt-L bond distance increases in the following order (mean values): $2.283( \pm 1) \AA(\mathrm{Pt}-\mathrm{P})<2.571( \pm 2) \AA\left(\mathrm{Pt}-\mathrm{Te}^{2}\right)<2.591( \pm 3) \AA\left(\mathrm{Pt}-\mathrm{Te}^{1}\right)<2.592( \pm 20) \AA\left(\mathrm{Pt}-\mathrm{Te}^{3}\right)$.

In another two complexes, namely $\left.\operatorname{Pt}\left(\eta^{3}-\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{~N}_{2} \mathrm{~S}_{2} \mathrm{~B}-\mathrm{S}^{1}, \mathrm{~B}^{1}, \mathrm{~S}^{2}\right)\left(\mathrm{PPh}_{3}\right)\right] \cdot 0.06 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ [13] and $\operatorname{Pt}\left(\eta^{3}-\mathrm{C}_{13} \mathrm{H}_{14} \mathrm{~N}_{5} \mathrm{~S}_{3} \mathrm{~B}-\right.$ $\left.\left.S^{1}, B^{1}, S^{2}\right)\left(P h_{3}\right)\right]{ }^{[14]}$, each $\eta^{3}$-ligand creates a pair of five-membered metallocyclic rings with a common central ligating $B^{1}$ atom of the $\mathrm{S}^{1} \mathrm{CNB}^{1} \mathrm{NCS}^{2}$ type. The values of the respective chelate angles are (mean values): $80.4( \pm 6)^{\circ}\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{B}^{1}\right)$ and $85.7( \pm 8)^{\circ}\left(\mathrm{B}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)$. The $\mathrm{PPh}_{3}$ demonstrated distorted square-planar geometry about the $\mathrm{Pt}(\mathrm{II})$ atom. The remaining $\mathrm{L}-$ Pt-L bond angles open in the following order (mean values): $95.9( \pm 5)^{\circ}\left(S^{2}-P t-P\right)<99.3( \pm 5)^{\circ}\left(S^{1}-P t-P\right)<162.4( \pm 1.0)^{\circ}$ $\left(\mathrm{S}^{1}-\mathrm{Pt}-\mathrm{S}^{2}\right)<174.4( \pm 2.2)^{\circ}\left(\mathrm{B}^{1}-\mathrm{Pt}-\mathrm{P}\right)$. The Pt-L bond distance increases in the following order (mean values): $2.110( \pm 19) \AA$ $\left(\mathrm{Pt}-\mathrm{B}^{1}\right)<2.284( \pm 10) \AA\left(\mathrm{Pt}-\mathrm{S}^{2}\right)<2.301( \pm 3) \AA\left(\mathrm{Pt}-\mathrm{S}^{1}\right)<2.382( \pm 2) \AA(\mathrm{Pt}-\mathrm{P})$.

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