

## REVIEW ARTICLE

# Heterotridentate Organodiphosphines in $Pt(\eta^3-P^1 P^2 X^1)(Y)$ ( $X^1 = N^1, C^1, Si^1$ ) Derivatives - Structural Aspects

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## Abstract

This review covers monomeric Pt(II) complexes of the compositions  $Pt(\eta^3-P^1 P^2 N^1)(Cl)$ ,  $Pt(\eta^3-P^1 P^2 C^1)(Cl)$ , and  $Pt(\eta^3-P^1 P^2 Si^1)(CH_3)$ . The structural parameters of the complexes (Pt-L, L-Pt-L) are analysed, compared with  $Pt(\eta^3-P^1 X^1 P^2)(Y)$  and discussed with an attention to the distortion of a square-planar geometry about the Pt(II) atoms as well as of trans-influence. The sums of Pt-L (x4) bond distances growing with covalent radius of the  $X^1$  atom. Generally, the inner coordination sphere about the Pt(II) atoms in  $Pt(\eta^3-P^1 P^2 X^1)(Y)$  derivatives is somewhat less crowded than in the analogous  $Pt(\eta^3-P^1 X^1 P^2)(Y)$  derivatives. There is a cooperative effect between a degree of distortion and trans-influence of  $X^1$  atom and its position in the metallocyclic rings.

**Keywords:** Structure; Heterotridentate; Organodiphosphines; Pt(II); Trans-Influence; Distortion

## Abbreviations

m (Bu <sup>t</sup> )(mes)P(CH <sub>2</sub> ) <sub>2</sub> P(Bu <sup>t</sup> )(η <sup>3</sup> -C <sub>9</sub> H <sub>10</sub> )	monoclinic 2-(t-butyl{2-[t-butyl(2,4,6-trimethylphenyl)-phosphanyl]ethyl}phosphanyl)-3,5-dimethyl-phenyl)methyl}triclinic
tr (Ph)(C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> )P <sup>1</sup> (CH <sub>2</sub> ) <sub>3</sub> P <sup>2</sup> . (C <sub>6</sub> H <sub>4</sub> N <sup>1</sup> H <sub>2</sub> )(Ph)(mes)P(η <sup>4</sup> - C <sub>10</sub> H <sub>9</sub> NO <sub>4</sub> ) <sub>2</sub> P(η <sup>2</sup> -C <sub>9</sub> H <sub>10</sub> )	(3,7-(1,5-bis(3,5-dicarboxyphenyl)-3-mesityl-7-(2-methylene-4,6-dimethylphenyl)-1,5-diazo-3,7-diphospho-cyclooctane))
(Me)(C <sub>9</sub> H <sub>4</sub> )(SiMe <sub>3</sub> ) <sub>7</sub> P <sup>1</sup> . (CH <sub>2</sub> ) <sub>2</sub> P <sup>2</sup> (Me)(η <sup>2</sup> -C <sub>9</sub> H <sub>4</sub> )	methyl-P,P-dimethyl-P,P'-bis(4-tris(trimethylsilyl)methyl-2,6-bis(bis(trimethylsilyl)-

(SiMe <sub>3</sub> ) <sub>6</sub> Si <sup>1</sup> (Me) <sub>2</sub>	methyl)phenyl)ethane-1,2-diphosphino)
(η <sup>1</sup> -C <sub>10</sub> H <sub>13</sub> O) <sub>2</sub> P(C <sub>15</sub> H <sub>12</sub> O)P.	(4,5-bis(bis(2-t-butylphenoxy)phosphino)-9,9-
(η <sup>1</sup> -C <sub>10</sub> H <sub>13</sub> O)(η <sup>2</sup> -C <sub>10</sub> H <sub>12</sub> O)	dimethylxanthene)(1-(dimethylsilyl))-2-(diphenyl-
	phosphino)-1,2-dicarbododicarboranehydrido-(1-
	(diphenylphosphino)-1,2-dicarbododicarborane

## Introduction

Platinum exists in a wide range of oxidation states from zero to +6 including non-integral Pt(2.25), Pt(2.5), Pt(2.87), Pt(3.25), and Pt(3.5). Of these, particularly in four and six-coordinate examples +2 and +4 oxidation states are the most common. The huge area of platinum coordination chemistry has been surveyed [1-3] with over 2000 examples.

Platinum (II) has a strong preference for square-planar coordination geometry. The high affinity of the platinum(II) ion for phosphorus enables it to bind effectively to organophosphines. Organophosphines as a soft P-donor ligand are very useful for building wide variety of platinum complexes. Recently, we classified and analysed structural data of over thirty monomeric platinum (II) complexes with heterotridentate organodiphosphines of composition Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y), (X<sup>1</sup> = O<sup>1</sup>, N<sup>1</sup>) [4]. Another reviews covers structural data for Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y), (X<sup>1</sup> = C<sup>1</sup>) [5]. Structural data for another over thirty examples of Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y), (X<sup>1</sup> = B<sup>1</sup>, S<sup>1</sup>, Si<sup>1</sup>) types were also analyzed [6].

The aim of this survey is to analyse structural parameters for Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y), (X<sup>1</sup> = N<sup>1</sup>, C<sup>1</sup>, Si<sup>1</sup>) derivatives. The data are correlated with those of analogous Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y), (X<sup>1</sup> = N<sup>1</sup>, C<sup>1</sup>, Si<sup>1</sup>) derivatives.

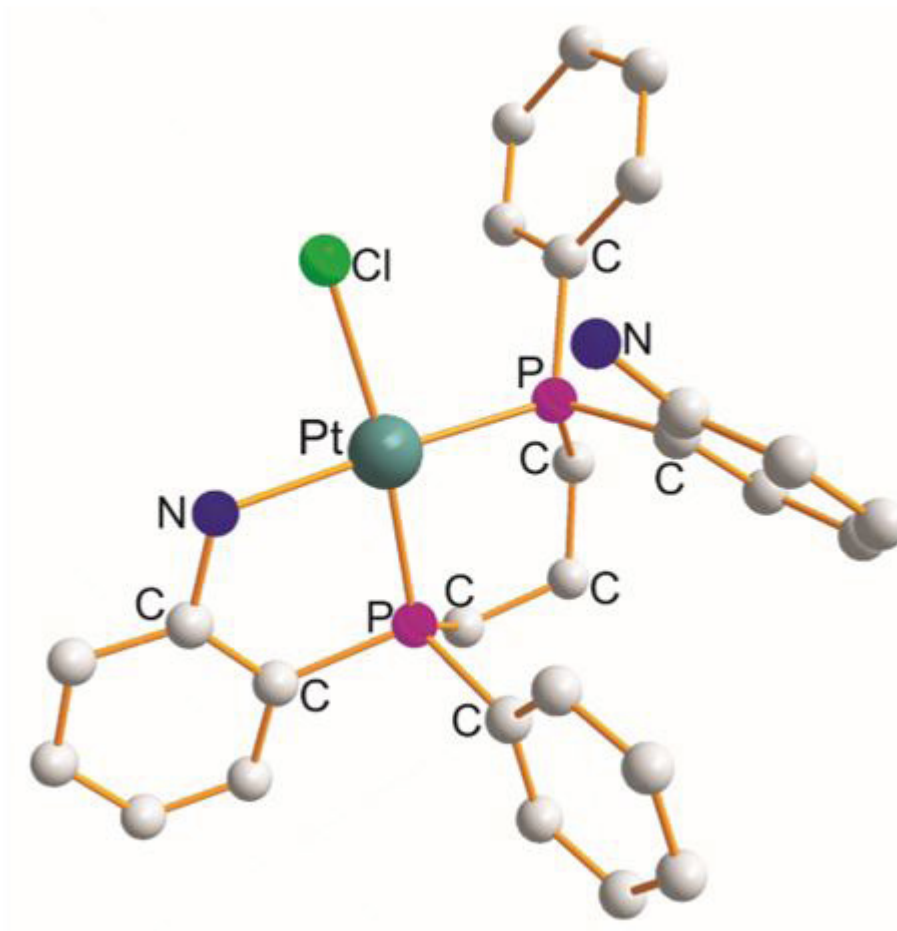
### Pt(η<sup>3</sup> - P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y) and Pt(η<sup>3</sup> - P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y) derivatives

Noticeable, while the former derivatives were studied sporadically, there are only five examples (Table 1) much more attention was paid to the other derivatives with over one hundred examples [4-6], and references therein. As far as we know, there is no paper with analysed structural data of such derivatives, this is the aim of this mini- review.

### Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>N<sup>1</sup>)(Cl) vs. Pt(η<sup>3</sup>-P<sup>1</sup>N<sup>1</sup>P<sup>2</sup>)(Cl) derivatives

In monoclinic [Pt{η<sup>3</sup>-(Ph)(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)P<sup>1</sup>(CH<sub>2</sub>)<sub>3</sub>P<sup>2</sup>(C<sub>6</sub>H<sub>4</sub>N<sup>1</sup>H<sub>2</sub>)(Ph)}(Cl)] (at 103 K) (Figure 1) [7], the tridentate P<sup>1</sup>P<sup>2</sup>N<sup>1</sup> - donor ligand can derive a six- and five-membered metallocyclic rings with common P<sup>2</sup> atom of the P<sup>1</sup>C<sub>3</sub>P<sup>2</sup>C<sub>2</sub>N<sup>1</sup> type with the values of chelate rings 93.0 (2)° (P<sup>1</sup> - Pt - P<sup>2</sup>) and 84.3(2)° (P<sup>2</sup> - Pt - N<sup>1</sup>). The values of the remaining L-Pt-L bond angles open in the order: 88.6(2)° (P<sup>1</sup>-Pt-Cl) < 92.4(2)° (N<sup>1</sup>-Pt-Cl) < 166.3(2)° (P<sup>1</sup>-Pt-N<sup>1</sup>) < 174.6(2)° (P<sup>2</sup>-Pt-Cl). The chloride completed a distorted square -planar geometry about Pt(II) atom. The Pt-L bond distance elongates in the sequence: 2.164(8) Å (Pt-N<sup>1</sup>, trans to P<sup>1</sup>) < 2.246(3) Å (Pt-P<sup>2</sup>, trans to Cl) < 2.298(3) Å (Pt-P<sup>1</sup>) < 2.393(3) Å (Pt-Cl). This is only example with such tridentate ligand.

There are thirteen examples of Pt(η<sup>3</sup>-P<sup>1</sup>N<sup>1</sup>P<sup>2</sup>)(Cl) derivative types. Their structural data were analysed [5]. The tridentate P<sup>1</sup>N<sup>1</sup>P<sup>2</sup> ligands can derive a variety of the metallocyclic rings with common N<sup>1</sup> atom. There are example with a pair of five-membered metallocycles of the types: P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>C<sub>2</sub>P<sup>2</sup>, [8-10] P<sup>1</sup>OCN<sup>1</sup>COP<sup>2</sup>, [11]; P<sup>1</sup>NCN<sup>1</sup>CNP<sup>2</sup>, [12] five- and six-membered P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>C<sub>3</sub>P<sup>2</sup> [13]; P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>NC<sub>2</sub>P<sup>2</sup> [14], metallocyclic rings with common N<sup>1</sup> atom. The chloride completed a distorted square-planar geometry about each Pt(II) atom. The Pt-L bond distance (mean values) elongates in the order: 2.024 Å (Pt-N<sup>1</sup>, trans to Cl) < 2.283 Å (Pt-P, mutually trans) < 2.307 Å (Pt-Cl). The L-Pt-L bond angles (mean values) open in the order: 83.7° (P<sup>1</sup>-Pt-N<sup>1</sup>/N<sup>1</sup>-Pt-P<sup>2</sup>) < 95.1° (P<sup>1</sup>-Pt-Cl/Cl-Pt-P<sup>2</sup>) < 167.0° (P<sup>1</sup>-Pt- P<sup>2</sup>) < 176.0° (N<sup>1</sup>-Pt-Cl).



**Figure 1:** Structure of  $[\text{Pt}\{\eta^3\text{-(Ph)(C}_6\text{H}_4\text{NH}_2\text{)P}^1\text{(CH}_2\text{)}_3\text{P}^2\text{(C}_6\text{H}_4\text{N}_1\text{H}_2\text{)(Ph)}\}\text{(Cl)}]$  (Ansell et al. 1985)

### $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{C}^1)(\text{Y})$ vs. $\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Y})$ derivatives

There are three examples of  $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{C}^1)(\text{Cl})$  complexes (Table 1). In monoclinic  $[\text{Pt}\{\eta^3\text{-(Bu}^t\text{)(mes)P(CH}_2\text{)}_2\text{P(Bu}^t\text{)(}\eta^2\text{-C}_9\text{H}_{10}\text{)}\}\text{(Cl)}].0.5\text{CH}_2\text{Cl}_2$  (at 100 K) [15]. Tridentate  $\text{P}^1\text{P}^2\text{C}^1$  ligand can derive a pair of five-membered metallocyclic rings with common  $\text{P}^2$  atom of the  $\text{P}^1\text{C}_2\text{P}^2\text{C}_2\text{C}^1$  type with the values of the chelate rings of  $87.0^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ ) and  $82.3^\circ$  ( $\text{P}^2\text{-Pt-C}^1$ ). The  $\eta^3$ -ligand with chloride build up a distorted square-planar geometry about Pt(II) atom. The remaining L-Pt-L bond angles open in the sequence  $89.3^\circ$  ( $\text{C}^1\text{-Pt-Cl}$ ) <  $101.1^\circ$  ( $\text{P}^1\text{-Pt-Cl}$ ) <  $163.2^\circ$  ( $\text{P}^1\text{-Pt-C}^1$ ) <  $171.5^\circ$  ( $\text{P}^2\text{-Pt-Cl}$ ). The P-L bond distance elongates in the sequence:  $2.087 \text{ \AA}$  ( $\text{Pt-C}^1$ , trans to  $\text{P}^1$ ) <  $2.188 \text{ \AA}$  ( $\text{Pt-P}^2$ , trans to Cl) <  $2.342 \text{ \AA}$  ( $\text{Pt-P}^1$ ) <  $2.383 \text{ \AA}$  ( $\text{Pt-Cl}$ ).

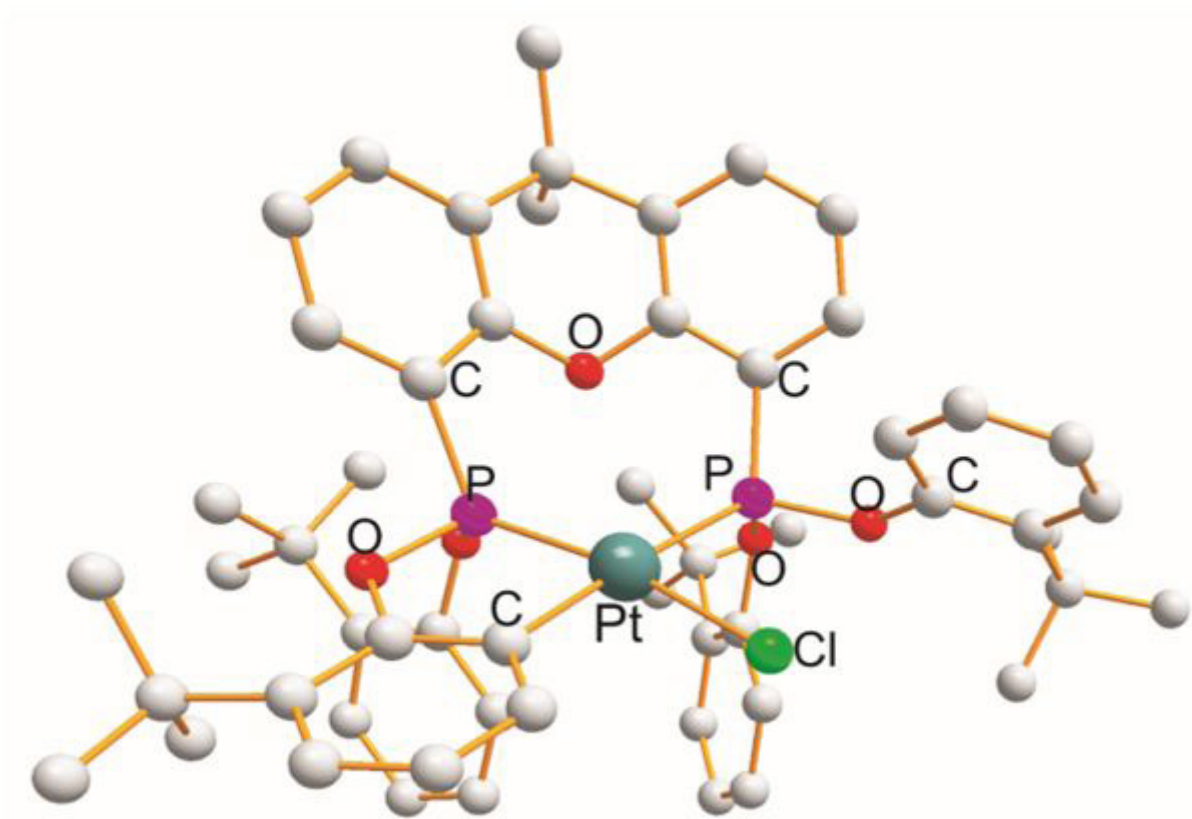
Structure of monoclinic  $[\text{Pt}\{\eta^3\text{-(}\eta^1\text{-C}_{10}\text{H}_{13}\text{O)}_2\text{P(C}_{15}\text{H}_{12}\text{O).P(}\eta^1\text{-C}_{16}\text{H}_{13}\text{O)(}\eta^2\text{-C}_{10}\text{H}_{12}\text{O)}\}\text{(Cl)}]$  (at 150 K) is shown in Figure 2 [16]. As can be seen the tridentate  $\text{P}^1\text{P}^2\text{C}^1$  ligand forms eight- and five-membered metallocyclic rings with common  $\text{P}^2$  atom of the  $\text{P}^1\text{C}_2\text{OC}_2\text{P}^2\text{OCC}^1$  type, with the values of the chelate rings of  $103.5^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ ) and  $79.8^\circ$  ( $\text{P}^2\text{-Pt-C}^1$ ). The  $\eta^3$ -ligand with chloride build up a distorted square-planar geometry about Pt(II) atom. The remaining L-Pt-L bond angles open in the sequence  $86.6^\circ$  ( $\text{P}^1\text{-Pt-Cl}$ ) <  $89.9^\circ$  ( $\text{C}^1\text{-Pt-Cl}$ ) <  $168.9^\circ$  ( $\text{P}^2\text{-Pt-Cl}$ ) <  $176.1^\circ$  ( $\text{P}^1\text{-Pt-C}^1$ ). The Pt-L bond distance elongates in the sequence:  $2.073 \text{ \AA}$  ( $\text{Pt-C}^1$ , trans to  $\text{P}^1$ ) <  $2.192 \text{ \AA}$  ( $\text{Pt-P}^2$ , trans to Cl) <  $2.341 \text{ \AA}$  ( $\text{Pt-Cl}$ ) <  $2.368 \text{ \AA}$  ( $\text{Pt-P}^1$ ).

COMPLEX	Space gr. Cryst. cl. Z	a [Å] b [Å] c [Å]	$\alpha$ [°] $\beta$ [°] $\gamma$ [°]	chromophore (chelate rings)	Pt-L <sup>b</sup> [Å]	L-Pt-L <sup>b</sup> [°]	Ref.
[Pt{ $\eta^3$ -(Ph) (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> )P <sup>1</sup> (CH <sub>2</sub> ) <sub>3</sub> P <sup>2</sup> (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ) (Ph) <sub>3</sub> (Cl)] (at 103 K)	m P2 <sub>1</sub> /c 4	12.704(2) 12.727(2) 20.727(3)	92.65(4)	PtP <sup>1</sup> P <sup>2</sup> N <sup>1</sup> Cl P <sup>1</sup> C <sub>3</sub> P <sup>2</sup> C <sub>2</sub> N <sup>1</sup>	P <sup>1</sup> 2.298(3) P <sup>2</sup> 2.246(3) N <sup>1</sup> 2.164(8) Cl 2.393(3)	P <sup>1</sup> ,P <sup>2</sup> 93.0(2) <sup>c</sup> P <sup>2</sup> ,N <sup>1</sup> 84.3 (2) <sup>d</sup> P <sup>1</sup> ,N <sup>1</sup> 166.3 (2) P <sup>1</sup> ,Cl 88.6 (2) N <sup>1</sup> ,Cl 92.4 (2) P <sup>1</sup> ,Cl 174.6 (2)	(Ansell et al. 1985)
[Pt{ $\eta^3$ -(Bu <sup>1</sup> )(Mes) P(CH <sub>2</sub> ) <sub>2</sub> P(Bu <sup>1</sup> )( $\eta^2$ - C <sub>9</sub> H <sub>10</sub> )}(Cl)].0.5CH <sub>2</sub> - Cl <sub>2</sub> (at 160 K)	m P2 <sub>1</sub> /c 4	11.153(3) 13.945(1) 20.869(1)	102.98(0)	PtP <sup>1</sup> P <sup>2</sup> C <sup>1</sup> Cl P <sup>1</sup> C <sub>2</sub> P <sup>2</sup> C <sub>2</sub> C <sup>1</sup>	P <sup>1</sup> 2.342 P <sup>2</sup> 2.188 C <sup>1</sup> 2.087 Cl 2.383	P <sup>1</sup> ,P <sup>2</sup> 87.0 <sup>d</sup> P <sup>2</sup> ,C <sup>1</sup> 82.3 <sup>d</sup> P <sup>1</sup> ,C <sup>1</sup> 163.2 P <sup>1</sup> ,Cl 101.1 P <sup>2</sup> ,Cl 171.5 C <sup>1</sup> ,Cl 89.3	(Clegg and Else- good 2017)
[Pt{ $\eta^3$ -( $\eta^1$ - C <sub>10</sub> H <sub>13</sub> O) <sub>2</sub> P(C <sub>15</sub> H <sub>12</sub> O) P( $\eta^1$ -C <sub>15</sub> H <sub>13</sub> O)( $\eta^2$ - C <sub>10</sub> H <sub>12</sub> O)}(Cl)]. CH <sub>2</sub> Cl <sub>2</sub> .0.5.pentane (at150 K)	m P2 <sub>1</sub> /c 4	9.483(0) 20.604(0) 21.441(0)	108.79(0)	PtP <sup>1</sup> P <sup>2</sup> C <sup>1</sup> Cl P <sup>1</sup> C <sub>2</sub> OC <sub>2</sub> P <sup>2</sup> OCC <sup>1</sup>	P <sup>1</sup> 2.368 P <sup>2</sup> 2.192 C <sup>1</sup> 2.073 Cl 2.341	P <sup>1</sup> ,P <sup>2</sup> 103.5 <sup>e</sup> P <sup>2</sup> ,C <sup>1</sup> 79.8 <sup>d</sup> P <sup>1</sup> ,C <sup>1</sup> 176.1 P <sup>1</sup> ,Cl 86.6 P <sup>2</sup> ,Cl 168.9 C <sup>1</sup> ,Cl 89.9	(van der Vlugt et al. 2003)
[Pt{ $\eta^3$ -(Mes)P( $\eta^4$ - C <sub>10</sub> H <sub>9</sub> NO <sub>4</sub> ) <sub>2</sub> P( $\eta^2$ - C <sub>9</sub> H <sub>10</sub> )}(Cl)].4 dmf (at 220 K)	tr Pī 2	13.175(2) 19.328(2) 16.222(2)	96.69(0) 98.78(0) 99.33(0)	PtP <sup>1</sup> P <sup>2</sup> C <sup>1</sup> Cl P <sup>1</sup> (CNC) <sub>2</sub> P <sup>2</sup> C <sub>2</sub> C <sup>1</sup>	P <sup>1</sup> 2.327 P <sup>2</sup> 2.162 C <sup>1</sup> 2.096 Cl 2.366	P <sup>1</sup> ,P <sup>2</sup> 84.3 <sup>d</sup> P <sup>1</sup> ,C <sup>1</sup> 84.0 <sup>d</sup> P <sup>1</sup> ,C <sup>1</sup> 168.3 P <sup>1</sup> ,Cl 102.3 P <sup>2</sup> ,Cl 172.9 C <sup>1</sup> ,Cl 89.2	(Karasik et al. 2006)
[Pt{ $\eta^3$ -(Me)P(C <sub>9</sub> H <sub>4</sub> ) (SiMe <sub>3</sub> ) <sub>7</sub> P <sup>1</sup> (CH <sub>2</sub> ) <sub>2</sub> . P <sup>2</sup> (Me)( $\eta^2$ -C <sub>9</sub> H <sub>4</sub> ) (SiMe <sub>3</sub> ) <sub>6</sub> Si <sup>1</sup> (Me) <sub>2</sub> } (CH <sub>3</sub> )] (at 93 K)	tr Pī 2	12.503(0) 12.681(0) 31.255(6)	83.08 (0) 82.16 (0) 62.04 (0)	PtP <sup>1</sup> P <sup>2</sup> Si <sup>1</sup> C P <sup>1</sup> C <sub>2</sub> P <sup>2</sup> C <sub>3</sub> Si <sup>1</sup>	P <sup>1</sup> 2.419 P <sup>2</sup> 2.275 Si <sup>1</sup> 2.321 C 2.117	P <sup>1</sup> ,P <sup>2</sup> 88.4 <sup>e</sup> P <sup>2</sup> ,Si <sup>1</sup> 93.6 <sup>d</sup> P <sup>1</sup> ,Si <sup>1</sup> 170.2 P <sup>1</sup> ,C 92.6 P <sup>2</sup> ,C 168.5 Si <sup>1</sup> ,C 83.6	(Tokitoh et al. 2009)

**Footnotes:**

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

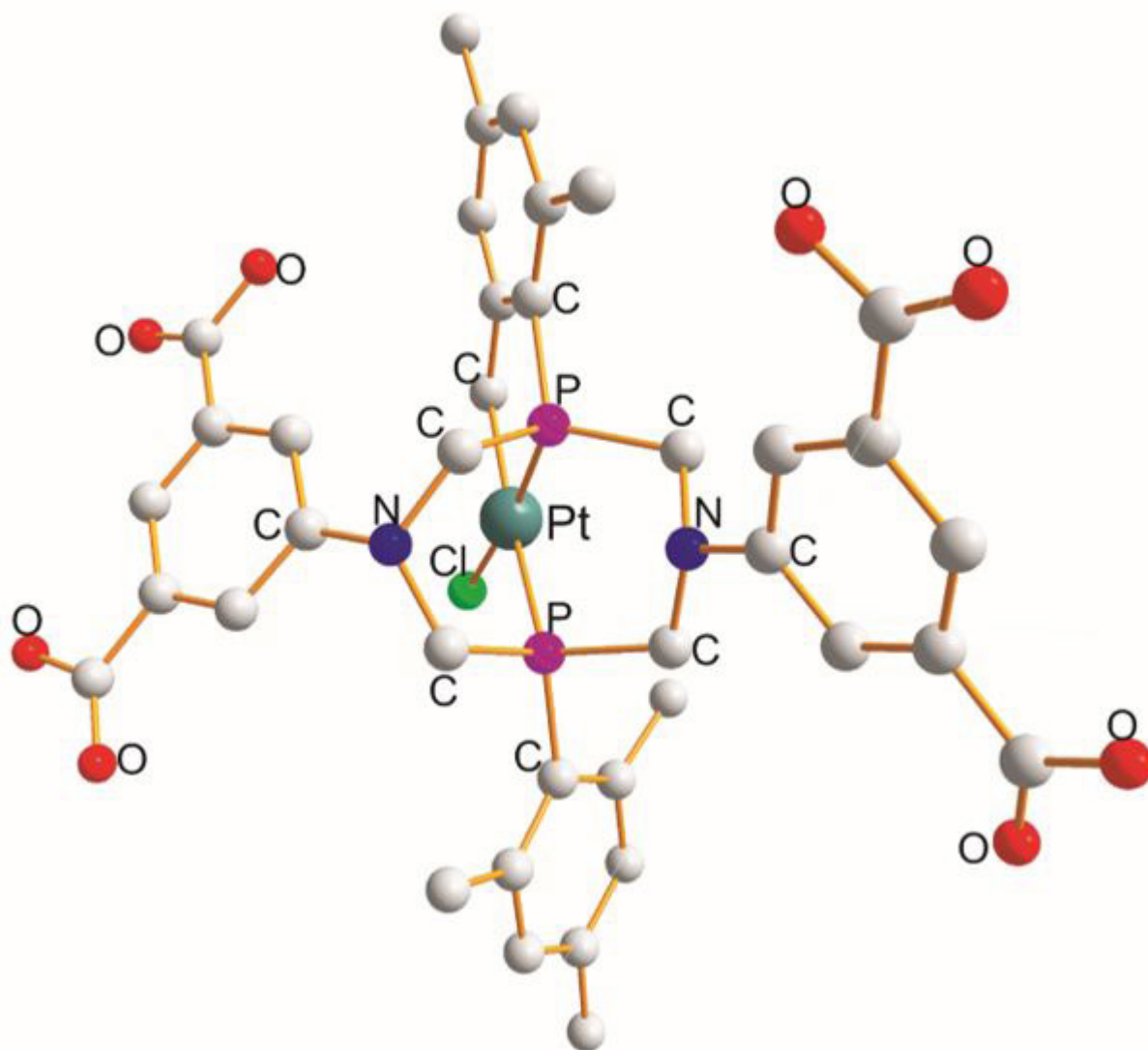
**Table 1:** Structural parameter for Pt( $\eta^3$ -P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y), (X<sup>1</sup> = N<sup>1</sup>, C<sup>1</sup>, Si<sup>1</sup>) derivatives<sup>a</sup>



**Figure 2:** Structure of  $[\text{Pt}\{\eta^3-(\eta^1\text{-C}_{10}\text{H}_{13}\text{O})_2\text{P}(\text{C}_{15}\text{H}_{12}\text{O})\text{P}(\eta^1\text{-C}_{16}\text{H}_{13}\text{O})(\eta^2\text{-C}_{10}\text{H}_{12}\text{O})\}](\text{Cl})$  (van der Vlugt et al. 2003)

In triclinic  $[\text{Pt}\{\eta^3-(\text{mes})\text{P}(\eta^4\text{-C}_{10}\text{H}_9\text{NO}_4)_2\text{P}(\eta^2\text{-C}_9\text{H}_{10})\}](\text{Cl})\cdot 4.\text{dmf}$  (at 220 K) [17] (Figure 3) the tridentate  $\text{P}^1\text{P}^2\text{C}^1$  ligand can derive a “double” six- and five-membered metallocyclic rings with common  $\text{P}^2$  atom of the  $\text{P}^1(\text{CNC})_2\text{P}^2\text{C}_2\text{C}^1$  type, with almost equal value of the chelate rings:  $84.3^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ ) and  $84.0^\circ$  ( $\text{P}^2\text{-Pt-C}^1$ ). The remaining L-Pt-L bond angles open in the order:  $89.2^\circ$  ( $\text{C}^1\text{-Pt-Cl}$ )  $<$   $102.3^\circ$  ( $\text{P}^1\text{-Pt-Cl}$ )  $<$   $168.3^\circ$  ( $\text{P}^1\text{-Pt-C}^1$ )  $<$   $172.9^\circ$  ( $\text{P}^2\text{-Pt-Cl}$ ). The Pt-L bond distance elongates in the order  $2.096 \text{ \AA}$  ( $\text{Pt-C}^1$ , trans to  $\text{P}^1$ )  $<$   $2.162 \text{ \AA}$  ( $\text{Pt-P}^2$ , trans to Cl)  $<$   $2.327 \text{ \AA}$  ( $\text{Pt-P}^1$ )  $<$   $2.366 \text{ \AA}$  ( $\text{Pt-Cl}$ ).

Much more attention was paid to  $\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Cl})$  derivatives. The tridentate  $\text{P}^1\text{C}^1\text{P}^2$  ligands can derive a variable combination of metallocycles with common  $\text{C}^1$  atom:  $\text{P}^1\text{C}_2\text{C}^1\text{C}_2\text{P}^2$  [18-20];  $\text{P}^1\text{OCC}^1\text{COP}^2$  [21,22];  $\text{P}^1\text{CPC}^1\text{PCP}^2$  [23];  $\text{P}^1\text{C}_2\text{C}^1\text{NCP}^2$  [24],  $\text{P}^1\text{C}_2\text{NC-}^1\text{NC}_2\text{P}^2$  [25], and  $\text{P}^1\text{NC}_2\text{C}^1\text{C}_2\text{NP}^2$  [26]. The tridentate  $\text{P}^1\text{C}^1\text{P}^2$  ligands with chloride build by a distorted square-planar geometry about Pt(II) atoms. The structural parameters of the complexes were analysed [6]. The L-Pt-L bond angles (mean values) open in the sequence  $83.0^\circ$  ( $\text{P}^1\text{-Pt-C}^1/\text{C}^1\text{-Pt-P}^2$ )  $<$   $95.0^\circ$  ( $\text{P}^1\text{-Pt-Cl}/\text{Cl-Pt-P}^2$ )  $<$   $165.0^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ )  $<$   $177.5^\circ$  ( $\text{C}^1\text{-Pt-Cl}$ ). The Pt-L bond distance (mean values) elongates in the order  $2.020 \text{ \AA}$  ( $\text{Pt-C}^1$ , trans to Cl)  $<$   $2.027 \text{ \AA}$  ( $\text{Pt-P}$ , mutually trans)  $<$   $2.388 \text{ \AA}$  ( $\text{Pt-Cl}$ , trans to  $\text{C}^1$ ).

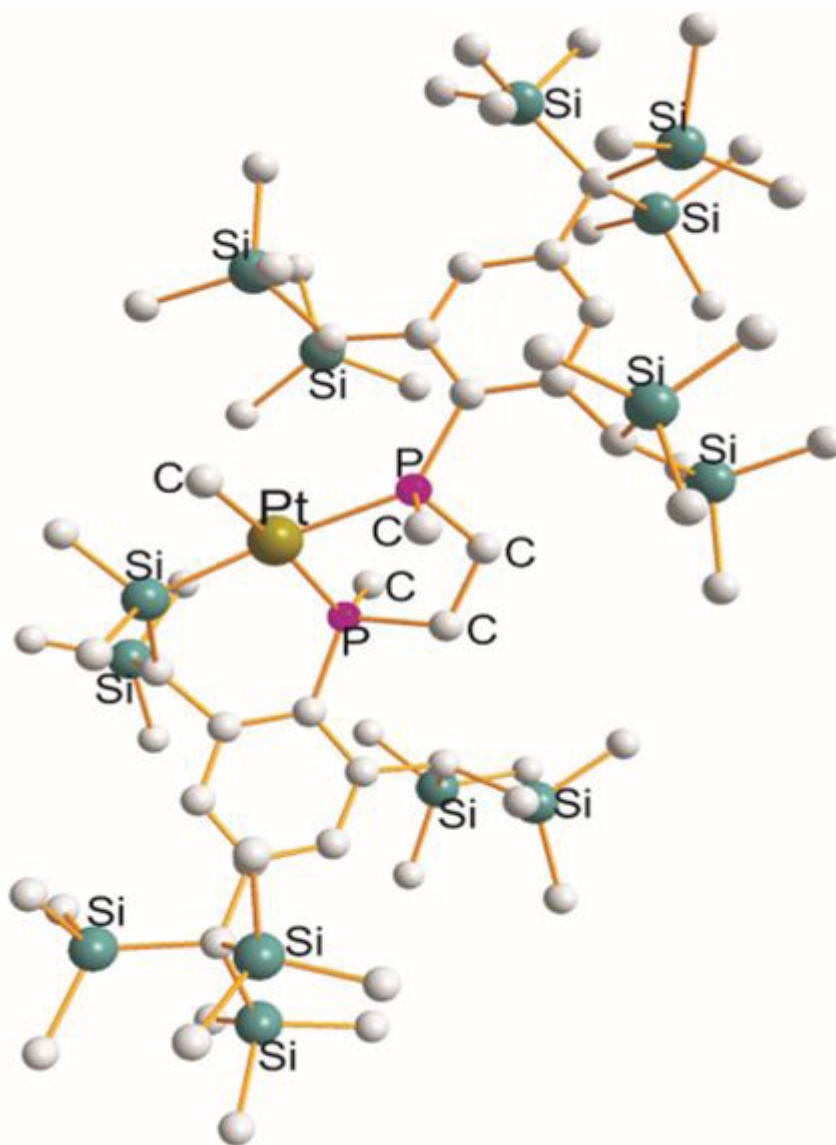


**Figure 3:** Structure of  $[\text{Pt}\{\eta^3\text{-(mes)P}(\eta^4\text{-C}_{10}\text{H}_9\text{NO}_4)_2\text{P}(\eta^2\text{-C}_9\text{H}_{10})\}(\text{Cl})]$  (Karasik et al. 2006)

### $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{Si}^1)(\text{Cl})$ vs. $\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Cl})$ derivatives

Triclinic  $[\text{Pt}\{\eta^3\text{-(Me)(C}_9\text{H}_4\text{)(SiMe}_3)_7\text{P}^1(\text{CH}_2)\text{P}^2(\text{Me})(\eta^2\text{-C}_9\text{H}_4\text{)(SiMe}_3)_6\text{Si}^1(\text{Me}_2)\}(\text{CH}_3)]$  (at 93 K) (Figure 4) [27] is the only example in which tridentate  $\text{P}^1\text{P}^2\text{Si}^1$  ligand with methyl group build up a distorted square-planar geometry about Pt(II) atom (Table 1). The tridentate ligand forms five- and six-membered metallocyclic rings with common  $\text{P}^2$  atom of the  $\text{P}^1\text{C}_2\text{P}^2\text{C}_3\text{Si}^1$  type, with the values of the respective angles of  $88.4^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ ) and  $93.6^\circ$  ( $\text{P}^2\text{-Pt-Si}^1$ ). The remaining L-Pt-L bond angles open in the sequence:  $83.6^\circ$  ( $\text{Si}^1\text{-Pt-C}$ ) <  $92.6^\circ$  ( $\text{P}^1\text{-Pt-C}$ ) <  $168.5^\circ$  ( $\text{P}^2\text{-Pt-C}$ ) <  $170.2^\circ$  ( $\text{P}^1\text{-Pt-Si}^1$ ). The Pt-L bond distance elongates in the sequence:  $2.117 \text{ \AA}$  ( $\text{Pt-C}$ , trans to  $\text{P}^2$ ) <  $2.275 \text{ \AA}$  ( $\text{Pt-P}^2$ ) <  $2.321 \text{ \AA}$  ( $\text{Pt-Si}^1$ ) <  $2.419 \text{ \AA}$  ( $\text{Pt-P}^1$ ).

Structural parameters are available for four  $\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Cl})$  derivatives [6]. Each tridentate  $\text{P}^1\text{Si}^1\text{P}^2$  ligand can derive a pair of five-membered metallocyclic rings with common Si atom of  $\text{P}^1\text{C}_2\text{Si}^1\text{C}_2\text{P}^2$  types [28-30] with the mean value of  $82.9^\circ$  ( $\text{P}^1\text{-Pt-Si}^1/\text{Si}^1\text{-Pt-P}^2$ ). The remaining L-Pt-L bond angles (mean values) open in the sequence:  $97.6^\circ$  ( $\text{P}^1\text{-Pt-C/C-Pt-P}^2$ ) <  $160.8^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ ) <  $173.0^\circ$  ( $\text{Si}^1\text{-Pt-C}$ ). The Pt-L bond distance (mean values) elongates in the sequence:  $2.112 \text{ \AA}$  ( $\text{Pt-C}$ , trans to  $\text{Si}^1$ ) <  $2.286 \text{ \AA}$  ( $\text{Pt-P}$ , mutually trans) <  $2.339 \text{ \AA}$  ( $\text{Pt-Si}^1$ ).



**Figure 4:** Structure of  $[\text{Pt}\{\eta^3\text{-(Me)(C}_9\text{H}_4\text{)(SiMe}_3\text{)}_7\text{P}_1(\text{CH}_2\text{)P}_2(\text{Me})(\eta^2\text{-C}_9\text{H}_4\text{)(SiMe}_3\text{)}_6\text{Si}_1(\text{Me}_2)\text{)}(\text{CH}_3)]$  (Tokitoh et al. 2009)

## Conclusions

In the chemistry of “soft” platinum is found in a wide variety of ligands forming a square-planar geometry about Pt(II) with varying degrees of distortion, and  $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{i}^1\text{X}^1)(\text{Y})$  and  $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$  derivatives are not an exception. Although platinum should preferentially bind to “soft” donor ligand in complexes studying a distorted square-planar geometries about Pt(II) atoms are build up with combination of “soft” (PL, SiL) and “hard” (NL, Cl) donor ligands. In  $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{X}^1)(\text{Y})$  derivative, the trans effect of  $\text{X}^1$  on Pt(II)- $\text{P}^1$  distance shortness the Pt- $\text{P}^1$  bond:  $2.349 \text{ \AA}$  ( $\text{Si}^1\text{-Pt } 2.232 \text{ \AA}$ ) <  $2.346 \text{ \AA}$  ( $\text{C}^1\text{-Pt } 2.065 \text{ \AA}$ ) <  $2.298 \text{ \AA}$  ( $\text{N}^1\text{-Pt } 2.164 \text{ \AA}$ ). The trans effect of Y on the Pt- $\text{P}^2$  distance increases the length (weakens), the trans bond:  $2.215 \text{ \AA}$  ( $\text{Cl-Pt } 2.379 \text{ \AA}$ ) <  $2.275 \text{ \AA}$  ( $\text{C-Pt } 2.122 \text{ \AA}$ ). This results suggest that in the former case is less transfer of donor electrons from  $\text{X}^1$  to Pt(II) than in the latter case. The total mean values of Pt-P bond distances are  $2.336 \text{ \AA}$  (Pt- $\text{P}^1$ ) and  $2.364 \text{ \AA}$  (Pt- $\text{P}^2$ ).

In  $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$  derivatives the Pt- $\text{X}^1$  bond distance (trans to Y) elongates in the order (mean values): Pt- $\text{C}^1$   $2.020 \text{ \AA}$  ( $\text{Cl-Pt } 2.388 \text{ \AA}$ ) < Pt- $\text{N}^1$   $2.024 \text{ \AA}$  ( $\text{Cl-Pt } 2.307 \text{ \AA}$ ) < Pt- $\text{Si}^1$   $2.339 \text{ \AA}$  ( $\text{C-Pt } 2.122 \text{ \AA}$ ). The Pt- $\text{P}^1$  (trans to  $\text{P}^2$ ) bond distance range from  $2.258$  to  $2.286 \text{ \AA}$  (average  $2.275 \text{ \AA}$ ).

The total sums of Pt-L (x4) bond distances of PtP<sup>1</sup>P<sup>2</sup>X<sup>1</sup>Y vs PtP<sup>1</sup>X<sup>1</sup>P<sup>2</sup>Y types are:

PtP<sup>1</sup>P<sup>2</sup>N<sup>1</sup>Cl, 9.101 Å vs. 8.897 Å, PtP<sup>1</sup>N<sup>1</sup>P<sup>2</sup>Cl

PtP<sup>1</sup>P<sup>2</sup>C<sup>1</sup>Cl, 8.973 Å vs. 8.953 Å, PtP<sup>1</sup>C<sup>1</sup>P<sup>2</sup>Cl

PtP<sup>1</sup>P<sup>2</sup>Si<sup>1</sup>C, 9.132 Å vs. 9.026 Å, PtP<sup>1</sup>Si<sup>1</sup>P<sup>2</sup>Cl

As can be seen, the total sums of Pt-L (x4) bond distances in the PtP<sup>1</sup>P<sup>2</sup>X<sup>1</sup>Y species are somewhat higher than the sums in PtP<sup>1</sup>X<sup>1</sup>P<sup>2</sup>Y species. This reflects how isomerism can alter the perception of the trans effect.

In Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y) derivatives each heterotridentate ligand forms two metallocyclic rings with common P<sup>2</sup> atom with varying numbers of atoms in the rings. Correspondingly, there is a variety of metallocyclic rings, and the effects of both steric and electronic factors can be seen from the values of the L-Pt-L bite angles. The angles opening in the sequence: P<sup>1</sup>(CNC)<sub>2</sub>P<sup>2</sup>/P<sup>2</sup>C<sub>2</sub>C<sup>1</sup> 84.3°/84.0° (168.3°) < P<sup>1</sup>C<sub>2</sub>P<sup>2</sup>/P<sup>2</sup>C<sub>2</sub>C<sup>1</sup> 87.0°/82.3° (169.3°) < P<sup>1</sup>C<sub>3</sub>P<sup>2</sup>/P<sup>2</sup>C<sub>2</sub>C<sup>1</sup> 93.0°/84.3° (177.3°) < P<sup>1</sup>C<sub>2</sub>P<sup>2</sup>/P<sup>2</sup>C<sub>3</sub>Si<sup>1</sup> 88.4°/93.6° (182.0°) < P<sup>1</sup>C<sub>2</sub>OC<sub>2</sub>P<sup>2</sup>/P<sup>2</sup>OCC<sup>1</sup> 103.5°/79.8° (187.8°).

As was already mentioned, there are over 120 examples of Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y) (X<sup>1</sup> = O<sup>1</sup>, N<sup>1</sup>, C<sup>1</sup>, S<sup>1</sup>, B<sup>1</sup>, Si<sup>1</sup>) derivatives which were analysed (Melnik, Mikuš 2021a,b, 2022). Therein, will be briefly outline Pt(η<sup>3</sup>-P<sup>1</sup>X<sup>1</sup>P<sup>2</sup>)(Y): X<sup>1</sup>/Y = N<sup>1</sup>/Cl (12 examples), X<sup>1</sup>/Y = C<sup>1</sup>/Cl (22 examples); X<sup>1</sup>/Y = Si<sup>1</sup>/C (4 examples); and X<sup>1</sup>/Y = Si<sup>1</sup>/H (2 examples) for comparison with analogous Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y).

In Pt(η<sup>3</sup>-P<sup>1</sup>N<sup>1</sup>P<sup>2</sup>)(Cl) the respective bite angles opening in the sequence: P<sup>1</sup>NCN<sup>1</sup>/N<sup>1</sup>C<sub>2</sub>P<sup>2</sup> 81.0°/81.1° (162.1°) < P<sup>1</sup>OCN<sup>1</sup>/N<sup>1</sup>COP<sup>2</sup> 82.1°/82.3° (164.4°) < P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>/N<sup>1</sup>C<sub>2</sub>P<sup>2</sup> 83.3°/82.7° (166.0°) < P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>/N<sup>1</sup>NC<sub>2</sub>P<sup>2</sup> 80.7°/91.2° (171.9°) < P<sup>1</sup>C<sub>2</sub>N<sup>1</sup>/N<sup>1</sup>C<sub>3</sub>P<sup>2</sup> 80.0°/95.1° (175.6°).

In Pt(η<sup>3</sup>-P<sup>1</sup>C<sup>1</sup>P<sup>2</sup>)(Cl) derivatives, the respective bite angles opening in the sequence: P<sup>1</sup>OCC<sup>1</sup>/C<sup>1</sup>COP<sup>2</sup> 80.0°/81.2° (161.2°) ~ P<sup>1</sup>C<sub>2</sub>C<sup>1</sup>/C<sup>1</sup>C<sub>2</sub>P<sup>2</sup> 82.2°/79.0° (161.2°) < P<sup>1</sup>NC<sub>2</sub>C<sup>1</sup>/C<sup>1</sup>C<sub>2</sub>NP<sup>2</sup> 84.0°/84.6° (168.6°) < P<sup>1</sup>CPC<sup>1</sup>PCP<sup>2</sup> 88.2°/88.6° (176.80°).

In Pt(η<sup>3</sup>-P<sup>1</sup>Si<sup>1</sup>P<sup>2</sup>)(Y) derivatives with only P<sup>1</sup>C<sub>2</sub>Si<sup>1</sup>/Si<sup>1</sup>C<sub>2</sub>P<sup>2</sup> type, the values are: 82.8°/83.0° (165.8°) for Y = CH<sub>3</sub> and for Y = H, the values are 84.3°/84.9° (169.2°).

In transition metal complexes, the oxidation state of metal plays a leading role in the geometry formed and platinum is no exception. In four-coordinate Pt(II) prefer a square-planar geometry. The utility of a simple metric to assess molecular shape and degree of distortion as well as exemplified best the T<sub>4</sub> parameter for a square-planar geometry by equation [31].

T<sub>4</sub> = 360 - (α + β) / 360 for square-planar, and

T<sub>4</sub> = 360 - (α + β) / 141 for tetrahedral

The values of T<sub>4</sub> range from 0.00 for the perfect square-planar geometry to 1.00 for a perfect tetrahedral geometry, since 360 - 2(109.5) = 141.

The total mean values of trans-L-Pt-L bond angles (α and β) as well as parameter T<sub>4</sub> for Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>X<sup>1</sup>)(Y) species are:

Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>N<sup>1</sup>)(Cl): 166.3° (P<sup>1</sup>-Pt-N<sup>1</sup>); 174.6° (P<sup>2</sup>-Pt-Cl); 0.030 (T<sub>4</sub>)

Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>C<sup>1</sup>)(Cl): 169.4° (P<sup>1</sup>-Pt-C<sup>1</sup>); 170.1° (P<sup>2</sup>-Pt-Cl); 0.051 (T<sub>4</sub>)

Pt(η<sup>3</sup>-P<sup>1</sup>P<sup>2</sup>Si<sup>1</sup>)(CH<sub>3</sub>): 170.2° (P<sup>1</sup>-Pt-Si<sup>1</sup>); 168.5° (P<sup>2</sup>-Pt-C); 0.059 (T<sub>4</sub>)



The values for  $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$  species are:

$\text{Pt}(\eta^3\text{-P}^1\text{N}^1\text{P}^2)(\text{Cl})$ :  $167.0^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ );  $176.4^\circ$  ( $\text{N}^1\text{-Pt-Cl}$ );  $0.046$  ( $\text{T}_4$ )

$\text{Pt}(\eta^3\text{-P}^1\text{C}^1\text{P}^2)(\text{Cl})$ :  $165.4^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ );  $177.2^\circ$  ( $\text{C}^1\text{-Pt-Cl}$ );  $0.048$  ( $\text{T}_4$ )

$\text{Pt}(\eta^3\text{-P}^1\text{Si}^1\text{P}^2)(\text{Cl})$ :  $160.8^\circ$  ( $\text{P}^1\text{-Pt-P}^2$ );  $173.0^\circ$  ( $\text{Si}^1\text{-Pt-C}$ );  $0.072$  ( $\text{T}_4$ )

The  $\text{Pt}(\eta^3\text{-P}^1\text{P}^2\text{X}^1)(\text{Y})$  complexes are somewhat more distorted than the  $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$  complexes, except  $\text{PtP}_2\text{SiC}$ , which is less distorted than  $\text{PtPSiPC}$  complexes.

We believe that such review as this, can continue to serve as useful function by centralizing valuable material and delineating areas worthy of future investigation.

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