Review Article

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Variable combinations of organophosphines in PtP_3X derivatives: Structural aspects

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Abstract: This review covers over fifty Pt (II) complexes of the compositions PtP_3X ($X = H, OL, NL, BL, Cl, SL, Br, \text{ or } I$). These complexes crystallized in three crystal classes: monoclinic (23 examples) triclinic (17 examples) and orthorhombic (11 examples). The PtP_3Cl is most common with 23 examples. There are variable combinations of organophosphines monodentate – P; bidentate– P,P; P,N; P,B; and tridentate – P,P,P; P,O,P; P,N,P; and P,S,P. The structural parameters (Pt–L, L–Pt–L) are analyzed 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-atoms.

Keywords: structure, organophosphines, PtP_3X , trans-influence

Abbreviations:

$Bu^tPB(C_6F_5)_2$ bis(pentafluorophenyl)boryl(di-
t-butyl)phosphine

$Bu^tP(PBu^t)_2PPBu^t$ (2,3,4-tri-t-butyl-1-
(t-butylphosphido)
cyklotetraphosphan-2-yl)

$(cy\text{-}hexyl)_2P(CH_2)_2P$
 $(cy\text{-}hexyl)_2$ 1,2-bis(dicyclohexylphosphine)
ethane

$(cy\text{-}hexyl)_2P(CH_2)_2P$
 $\{(CH_2CH_2P(=O)$
 $(cy\text{-}hexyl)_2(CH_2)_2P$
 $(cy\text{-}hexyl)_2$ ((2-(dicyclohexyl-
phosphanoyl)ethyl)bis(2-
(dicyclohexylphosphanyl)ethyl)
phosphene

$(cy\text{-}hexyl)_2PB(C_6F_5)_2$ (bis(pentafluorophenyl)boryl)
(dicyclohexyl)phosphine

$(\eta^1\text{-}C_{28}H_{45})$
 $P(=CH(C_5H_3N)=CH)$
 $P(\eta^1\text{-}C_{28}H_{45})$ (2,6-bis{[(1,1,3,3,5,5,7,7-octaethyl-
1,2,3,4,5,6,7-hexahydro-3-
indacen-4-yl)phosphanylidene]
methyl}pyridine)

$(\eta^2\text{-}C_6H_{12})P(1,2\text{-}C_6H_4)P$
 $(\eta^2\text{-}C_6H_{12})$ 1,2-bis(2,5-dimethylphosphatano)
benzene

$(\eta^2\text{-}C_6H_{12})P(C_6H_4)P$
 $(\eta^2\text{-}C_6H_{12})$ 1,2-bis(2,5-dimethylphosphanyl)
benzene

$Et_2P(CH_2)_2PEt_2$ 1,2-bis(diethylphosphino)
ethane

$(Me)(Ph)P(C_6H_4)\{P(Ph)$
 (Me) 1,2-bis(methylphenylphosphino)
benzene

$Me_2P(OB(F_2)OPMe_2$ bis(dimethylphosphino)
difluoroborate

$P(=O)(Me)(C_{15}H_{23})$ methyl(2,4,6-tri-
isopropylphenyl)oxophosphanyl

$P(BH_3)Ph_2$ boryl(diphenyl)phosphine

$P(C_{15}H_{23})Ph$ phenyl(2,4,6-tri-
isopropylphenyl)phosphide

$P(C_{18}H_9)Ph_2$ 1-(diphenylphosphino)pyrene

$P(Me)(C_{15}H_{23})$ methyl(2,4,6-tri-
isopropylphenyl)phosphide

$P(Me)_2Ph$ dimethylphenylphosphine

PBu^t_3 tri-t-butylphosphine

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$\text{Ph}_2\text{P}(\text{C}_{12}\text{H}_8\text{O})\text{PPh}_2$	oxybis(2,1-phenylene) bis(diphenylphosphine)
$\text{Ph}_2\text{P}(\text{C}_{14}\text{H}_{12}\text{OSi})\text{PPh}_2$	(10,10-dimethyl-1,4- phenoxasilene-4,6-diyl)bis diphenylphosphine)
$\text{Ph}_2\text{P}(\text{C}_{15}\text{H}_{12}\text{O})\text{PPh}_2$	bis(diphenylphosphine) (9,9dimethyl-9H-xanthene-4, 5-diyl)
$\text{Ph}_2\text{P}(\text{C}_{20}\text{H}_{12})\text{PPh}_2$	bis(diphenylphosphine) binaphthalene-2,2-etiyl
$\text{Ph}_2\text{P}(\text{C}_{26}\text{H}_{23}\text{OP})\text{P}(\text{Ph})$ $(\text{C}_{26}\text{H}_{23}\text{OP})\text{PPh}_2$	((phenylphosphanediy)l bis[1-(diphenyl-phosphanyl) ethane-2,1-diyl]]-bis[diphenyl- phosphane oxide])
$\text{Ph}_2\text{P}(\text{C}_2\text{B}_9\text{H}_{10})\text{PPh}_2$	7,8-bis(diphenylphosphino)-7,8- dicarbamido-undecaborate
$\text{Ph}_2\text{P}(\text{C}_4\text{H}_4\text{NO})\text{PPh}_2$	bis(2-bis(diphenylphosphino) methylidene)-1,3-oxazolidinido
$\text{Ph}_2\text{P}(\text{C}_5\text{H}_4\text{N})$	2-(diphenylphosphino)pyridine
$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\{\text{N}(\text{CH}_2)_2\text{N}\}$ $\text{P}(\text{C}_6\text{H}_4)_2\text{PPh}_2$	(1,3-bis(2-(diphenylphosphino) phenyl)-1,3,2- diazaphospholidine)
$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\{\text{N}(\text{CH}_2)_2\text{N}\}$ $\text{P}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2$	(1,3-bis(2-(diphenylphosphino) phenyl)-2-methyl-1,3,2- diazaphospholidine)
$\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(=\text{O})(\text{C}_6\text{H}_4)$ PPh_2	(sulfinyldi-2,1-phenylene)bis (diphenylphosphine)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})$ $(\text{CH}_2)_2\text{PPh}_2$	bis(2-diphenylphosphinoethyl) phenylphosphine
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}(\text{Ph})$ $(\text{CH}_2)_3\text{PPh}_2$	bis(3-diphenylphos phinopropyl)phenylphosphine
$\text{Ph}_2\text{PN}(\text{H})\text{PPh}_2$	bis(diphenylphosphino)amine
PMe_3	trimethylphosphine
PPh_3	triphenylphosphine
$\text{Pr}_2^i\text{P}(\text{C}_{11}\text{H}_8)\text{P}(\text{Pr}^i)(\text{C}_{11}\text{H}_8)$ PPr_2^i	((isopropylphosphinediyl) bis(1,2-di-hydro-6,5-diyl)bis(- isopropylphosphine))
$\text{Pr}_2^i\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{C}_6\text{H}_4)\text{PPr}_2^i$	((phosphinediyl)di-2,1- phenylene)-bis(di- isopropylphosphinato)
$\text{SC}_6\text{F}_4(\text{CF}_3)$	2,3,5,6 -tetrafluoro-4-(trifluoro methyl)benzenethiolate

SC_6HF_4	2,3,5,6 -tetrafluorobenzenethiolate
SPh	benzenethiolate
tpbp	1,3,5-triphosphabicyclo[2.1.0]- pentin-2-ene

1 Introduction

The high affinity of the platinum(II) ion for phosphorous enables it to bind effectivity to organophosphines. There are numerous published structural studies on platinum complexes which were classified and analyzed (Holloway and Melník, 2002, 2003, 2004). Research activity on this field is always very active. Organophosphines as a soft P-donor ligands are very useful for building wide variety of platinum complexes. Recently, we classified and analyzed structural data of monomeric organoplatinum complexes with PtP_3C inner coordination sphere (Melník and Mikuš, 2017). Another review covers structural data of monomeric platinum(II) coordination complexes with an inner coordination spheres. PtP_4 , PtP_3X ($\text{X} = \text{H}, \text{F}, \text{O}, \text{N}, \text{Cl}, \text{S}, \text{Br}, \text{or I}$) and PtP_2X_2 ($\text{X} = \text{H}, \text{F}, \text{O}, \text{N}, \text{CN}, \text{or B}$) in which P-donor ligands are monodentate organomonophosphines (Melník and Mikuš, 2015).

The aim of this survey is to correlate the structural parameters available, for PtP_3X ($\text{X} = \text{H}, \text{OL}, \text{NL}, \text{BL}, \text{Cl}, \text{SL}, \text{Br}, \text{or I}$) derivatives with variable combinations of organophosphines. The data are comparing and discuss with PtP_3X in which P-donor ligands are only monodentate organomonophosphines.

2 PtP_3X derivatives

There are over fifty examples, in which the inner coordination spheres about the Pt (II) atoms of the composition PtP_3X are formed by variable combinations of organophosphines and X atoms.

2.1 PtP_3H type

There are five examples of this type. In orthorhombic dark red $[\text{Pt}(\eta^2\text{-P}_7)(\text{PPh}_3)(\text{H})][\text{K}(2,2,2\text{-cryptate})]_2$ (Charles et al., 1996), the chelating P_7 ligand creates four-membered metallocyclic ring with the value of $\text{P}^1\text{-Pt-P}^2$ bite angle of $78.2(4)^\circ$ (P^1PP^2). The mean value of the remaining cis-P-Pt-P bond angles is 98.0° , and trans- $\text{P}^1\text{-Pt-P}^3$ bond angle is 174.5° . The Pt-P bond distances

are: 2.42(1) Å (Pt–P², trans to H), 2.40(1) Å (Pt–P¹), and 2.23(1) Å (Pt–PPh₃).

In another three examples two monoclinic [Pt{η²-Et₂P(CH₂)₂PEt₂}[P(BH₃)Ph₂](H)] (at 150 K) (Jaska et al., 2003), [Pt{η²-(cy-hexyl)₂P(CH₂)₂P(cy-hexyl)₂}[P(BH₃)Ph₂](H)] (at 150 K) (Jaska et al., 2005) and orthorhombic [Pt{η²-(η²-C₆H₁₂)P(C₆H₄)P(η²-C₆H₁₂)}[P(C₁₅H₂₃)Ph](H)] (at 238 K) (Kovacik et al., 2000), each chelating-P¹,P² ligand creates five-membered metallocyclic ring with the values of P¹–Pt–P² bite angles of 86.0° and 87.1° (Jaska et al., 2003), 87.1° (Jaska et al., 2005), and 86.9° (Kovacik et al., 2000) (P¹C₂P²). The monodentate P³R₃ with hydride completed a distorted square-planar geometry about Pt(II) atoms. The remaining L–Pt–L bond angles open in the sequence: (mean values): 82.7(±0.5)° (P³–Pt–H) < 91.0(±1.9)° (P¹–Pt–H) < 100.0(±3.2)° (P²–Pt–P³) < 171.8(±2.6)° (P²–Pt–H). The Pt–L distance elongate in the sequence (mean values): 1.65(±0.6) Å (Pt–H) < 2.251(±0.02) Å (Pt–P¹) < 2.302(±0.01) Å (Pt–P², trans to H) < 2.328(±0.01) Å (Pt–P³).

In triclinic [Pt{η²-Ph₂P(C₂₀H₁₂)PPh₂}(PMe₃)(H)]BF₄ (Figure 1) (Campbell and Gagne, 2007), the chelating P¹P² ligand creates seven membered metallocyclic ring with the value of P¹–Pt–P² bite angle of 97.9° (P¹C₄P²). The P³Me₃ with hydride completed inner coordination sphere about Pt(II) atom. The remaining L–Pt–L bond angles open in the sequence: 66.1° (P³–Pt–H) < 101.8° (P¹–Pt–H) < 171.4° (P²–Pt–H). The Pt–L bond distance elongate in the

sequence: 1.63 Å (Pt–H) < 2.113 Å (Pt–P¹) < 2.306 Å (Pt–P², trans to H) < 2.322 Å (Pt–P³).

2.2 PtP₃O type

There are three examples of this type. In triclinic [Pt{η³-Ph₂P(CH₂)₂P(Ph)(CH₂)₂PPh₂}(ONO₂)](NO₃) (Fernandez et al., 2001) and monoclinic [Pt{η³-Ph₂P(CH₂)₂P(Ph)(CH₂)₂PPh₂}{OS(=O)₂CF₃}}(O₃SCF₃) (Annibale et al., 2000) the tridentate P¹,P²,P³-donor ligand creates a pair of five-membered metallocyclic rings with the common P² atom of the type P¹C₂P²C₂P³, with the mean value of P¹–Pt–P²/P²–Pt–P³ angles of 84.3(±1.7)°. The mean value of the remaining L–Pt–L bond angles are: 166.0(±1.4)° (P¹–Pt–P³), 95.3(±4.8)° (P¹–Pt–O/P³–Pt–O), and 173.7(±2.1)° (P²–Pt–O). The mean value of Pt–L bond distance elongate in the sequence: 2.109(±0.7) Å (Pt–O) < 2.196(±0.011) Å (Pt–P², trans to O) < 2.318(±0.006) Å (Pt–P^{1,3}, trans to P).

In monoclinic [Pt{η³-Ph₂P(C₁₅H₁₂O)PPh₂}[PPh₂(C₅H₄N)]](O₃SCF₃)₂·0.5H₂O (at 150 K) (Figure 2) (Lenero et al., 2013) tridentate-P¹, O¹, P² donor ligand creates a pair of five-membered metallocycles with common O¹ atom of the P¹C₂O¹C₂P² type, with the mean value of P¹–Pt–O¹/O¹–Pt–P² angles of 81.6(±0.7)°. The values of the remaining L–Pt–L bond angles are: 98.5(±1.7)° (P¹–Pt–P³/P²–Pt–P³), 162.2° (P¹–Pt–P²), and 174.8° (O¹–Pt–P³). The Pt–L bond distance

Figure 1: Structure of [Pt{η²-Ph₂P(C₂₀H₁₂)PPh₂}(PMe₃)(H)]⁺ (Campbell and Gagne, 2007).

Figure 2: Structure of [Pt{η³-Ph₂P(C₁₅H₁₂O)PPh₂}[P(C₅H₄N)(Ph)₂]]²⁺ (Lenero et al., 2013).

elongate in the sequence: 2.189 Å (Pt–O) < 2.239 Å (Pt–P³, trans to O) < 2.305(±0.07) Å (Pt–P¹, Pt–P²).

2.3 PtP₃N type

There are four examples of this type. In triclinic [Pt{η³-(η¹-C₂₈H₄₅)P(=CH(C₅H₃N)CH=)P(η¹-C₂₈H₄₅)}(PPh₃)₂]2CH₂Cl₂ (at 103 K) (Takeuchi et al., 2016) tridentate P¹,N¹,P²- donor ligand creates a pair of five-membered metallocycles with common N¹ atom of the P¹C₂N¹C₂P² type, with the mean value of P¹–Pt–N¹/N¹–Pt–P² bond angles of 81.0(±0.5)°. The values of the remaining L–Pt–L bond angles are: 98.2(±2.1)° (P¹–Pt–P³R₃, P²–Pt–P³), 158.7° (P¹–Pt–P²), and 173.0°(N¹–Pt–P³). The Pt–L bond distance elongate in the sequence: 2.082 Å (Pt–N) < 2.270 Å (Pt–P³, trans to N) < 2.313(±0.012) Å (Pt–P¹, Pt–P²).

In monoclinic [Pt{η²-Ph₂P(C₄H₄NO)PPh₂-P¹,P²}{η²-Ph₂P(C₄H₄NO)PPh₂-P³,N}}]·CH₂Cl₂ (at 173 K) (Figure 3) (Zhang et al., 2011) a distorted square-planar arrangement about the Pt(II) atom is build up by two chelating ligands one homo- via P¹,P² – and another one hetero – via P³,N atoms. The former creates four-membered metallocycle with the value of P¹–Pt–P² bite angle of 71.0° (P¹CP²) and the latter forms five-membered metallocycle with the value of P³–Pt–N bite angle of 80.9° (P³C₂N). The remaining L–Pt–L bond angles open in the order: 102.8° (P²–Pt–N) < 105.2° (P¹–Pt–P³) < 173.4° (P¹–Pt–N) < 176.0° (P²–Pt–P³). The Pt–L

bond distance elongate in sequence: 2.047 Å (Pt–N) < 2.270 Å (Pt–P¹, trans to N) < 2.230 Å (Pt–P²) < 2.322 Å (Pt–P³).

In remaining two examples, triclinic [Pt{η²-Ph₂P(C₁₂H₈O)PPh₂-P¹,P²}{η²-Ph₂P(C₅H₄N)-P³,N}}](O₃SCF₃)₂·3CH₂Cl₂ (at 150 K), and monoclinic [Pt{η²-Ph₂P(C₁₄H₁₂OSi)PPh₂-P¹,P²}{η²-Ph₂P(C₅H₄N)-P³,N}}](O₃SCF₃)·CH₂Cl₂ (at 180 K) (Lenero et al., 2013) a distorted square-planar arrangement about each Pt(II) atom is build up by homo-chelating ligand via P¹,P²- donor atoms and hetero-chelating ligand via P³,N donor atoms. Each homo-chelating ligand creates eight-membered metallocycle (P¹C₂O¹C₂P²) and hetero-chelating creates four-membered metallocycle (P³CN). The mean values of the respective metallocycles are: 94.4(±2.0)° (P¹–Pt–P²) and 69.1(±0.1)° (P³–Pt–N). The remaining L–Pt–L bond angles open in the sequence (mean values): 94.4(±2.1)° (P³–Pt–N) < 99.3(±0.1)° (P¹–Pt–P²) < 161.1(±3.8)° (P¹–Pt–P³) < 168.3(±0.2)° (P²–Pt–N). The Pt–L bond distance elongate in the sequence (mean values): 2.111(±0.1) Å (Pt–N) < 2.272(±0.007) Å (Pt–P², trans to N) < 2.336(±0.017) Å (Pt–P¹, Pt–P³).

2.4 PtP₃B type

Two triclinic complexes are of this type. Both complexes: [Pt{η²-Bu^tPB(C₆F₅)₂}(PPh₃)₂] (at 193 K) and [Pt{η²-(cy-hexyl)₂PB(C₆F₅)₂}(PPh₃)₂] (at 193 K) (Figure 4) (Amgoune et al., 2012) are isostructural. The inner coordination sphere

Figure 3: Structure of [Pt{η²-Ph₂P(C₄H₄NO)PPh₂-P¹,P²}{η²-Ph₂P(C₄H₄NO)PPh₂-P³,N}}] (Zhang et al., 2011).

Figure 4: Structure of [Pt{η²-(cy-hexyl)₂PB(C₆F₅)₂}(PPh₃)₂] (Amgoune et al., 2012).

about each platinum atom is build up by heterobidentate donor ligand via P,B donor atoms and two monodentate PPh_3 ligands completed distorted tetrahedral geometry (PtP_3B). Each heterobidentate ligand creates three membered metallocyclic ring with mean $\text{P}^1\text{--Pt--B}$ bite angles of $49.6(\pm 0.4)^\circ$ (P^1B). The remaining L--Pt--L bond angles open in the sequence (mean values): $101.4(\pm 0.5)^\circ$ ($\text{P}^2\text{--Pt--P}^3$) < $101.6(\pm 1.5)^\circ$ ($\text{P}^3\text{--Pt--B}$) < $109.0(\pm 0.1)^\circ$ ($\text{P}^1\text{--Pt--P}^2$) < $148.0(\pm 1.5)^\circ$ ($\text{P}^1\text{--Pt--P}^3$) < $156.5(\pm 2.5)^\circ$ ($\text{P}^2\text{--Pt--B}$). The Pt--L bond distance elongate in the sequence (mean values): $2.262(\pm 0.028)$ Å (Pt--B) < $2.310(\pm 0.012)$ Å (Pt--P^1) < $2.319(\pm 0.023)$ Å (Pt--P^3) < $2.356(\pm 0.018)$ Å (Pt--P^2 , trans to B).

Figure 5: Structure of $[\text{Pt}\{\eta^2\text{-Bu}^1\text{P}^1(\text{PBu}^1)_2\text{PP}^2\text{Bu}^1\}\{\text{P}^3(\text{Me})_2\text{Ph}\}\text{Cl}]$ (Gomez-Ruiz et al., 2007).

2.5 PtP_3Cl type

In two colorless one triclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{PN}(\text{CH})\text{PPh}_2\}\{\text{P}(\text{Me})_2\text{Ph}\}\text{Cl}]\text{Cl}$ and orthorhombic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{PN}(\text{H})\text{PPh}_2\}(\text{PBu}^t)_3]\text{Cl}]\text{Cl}$ (Bhattacharya et al., 1993) a distorted square-planar environment about each $\text{Pt}(\text{II})$ atom is build up by chelating P^1, P^2 - donor ligand, with P^3R_3 donor ligand and chlorine. The chelating ligand creates four-membered metallocycle with the mean value of $\text{P}^1\text{--Pt--P}^2$ bite angle of $69.8(\pm 0.2)^\circ$ (P^1NP^2). The mean values of remaining cis- L--Pt--L bond angles are: $102.8(\pm 1.1)^\circ$ (P--Pt--P) and $93.6(\pm 5.3)^\circ$ ($\text{P}^3\text{--Pt--Cl}$). The Pt--L bond distance elongate in the sequence (mean values): $2.228(\pm 0.001)$ Å (Pt--P^2 , trans to Cl) < $2.305(\pm 0.008)$ Å (Pt--P^1) < $2.331(\pm 0.001)$ Å (Pt--P^3) < $2.351(\pm 0.005)$ Å (Pt--Cl).

In two monoclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}\{\text{P}(\text{cycloenH})_2\}\text{Cl}](\text{BF}_4)_2 \cdot \text{MeCN}$ (Khasnis et al., 1992), $[\text{Pt}\{\eta^2\text{-tpbp}\}(\text{PEt}_3)_2\text{Cl}]$ (Caliman, 1998) and triclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}\{\text{P}(\text{C}_6\text{H}_5)_2\text{Ph}\}\text{Cl}]\text{CF}_3\text{SO}_3 \cdot \text{CH}_2\text{Cl}_2$ (Hu et al., 2009) each chelating P^1, P^2 ligand creates four-membered metallocyclic ring with the mean value of $\text{P}^1\text{--Pt--P}^2$ bite angle of $71.5(\pm 0.4)^\circ$ (P^1CP^2). The remaining L--Pt--L bond angles are: $97.8(\pm 2.4)^\circ$ (P--Pt--P), $168.2(\pm 0.1)^\circ$ (P--Pt--P), $95.1(\pm 2.0)^\circ$ (P--Pt--Cl), and $166.3(\pm 1.8)^\circ$ (P--Pt--Cl). The Pt--L bond distance elongate in the sequence (mean values): $2.255(\pm 0.008)$ Å (Pt--P^2 , trans to Cl) < $2.315(\pm 0.016)$ Å (Pt--P^1) < $2.319(\pm 0.003)$ Å (Pt--P^3) < $2.360(\pm 0.02)$ Å (Pt--Cl).

In monoclinic $[\text{Pt}\{\eta^2\text{-Bu}^1\text{P}^1(\text{PBu}^1)_2\text{PP}^2\text{Bu}^1\}\{\text{P}^3(\text{Me})_2\text{Ph}\}\text{Cl}]$ (at 223 K) (Figure 5) (Gomez-Ruiz et al., 2007), the chelating ligand creates four-membered metallocyclic ring with the value of $\text{P}^1\text{--Pt--P}^2$ bite angle of 79.9° (P^1PP^2). The values of the remaining cis- L--Pt--L bond angles open in the sequence: 85.9° ($\text{P}^3\text{--Pt--Cl}$) < 96.8° ($\text{P}^1\text{--Pt--Cl}$) < 97.7° ($\text{P}^1\text{--Pt--P}^3$), and trans- $\text{P}^2\text{--Pt--Cl}$ bond angle is 175.3° . The Pt--L bond distance elongate in the sequence: 2.301 Å

(Pt--P^2 , trans to Cl) < 2.309 Å (Pt--P^1) < 2.327 Å (Pt--P^3) < 2.415 Å (Pt--Cl).

There are six examples: triclinic $[\text{Pt}\{\eta^2\text{-(Me)}(\text{Ph})\text{P}(\text{C}_6\text{H}_4)\}\{\text{P}(\text{Ph})(\text{Me})\}\{\text{P}(\text{H})(\text{Me})(\text{Ph})\}\text{Cl}]\text{PF}_6 \cdot \text{CH}_2\text{Cl}_2$ (Bader et al., 1992, 1995), monoclinic $[\text{Pt}\{\eta^2\text{-(C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\eta^2\text{-C}_6\text{H}_5)_2\}\{\text{P}(\text{O})(\text{Me})(\text{C}_{15}\text{H}_{23})\}\text{Cl}]\cdot 0.5\text{toluene}$ (at 208 K), orthorhombic $[\text{Pt}\{\eta^2\text{-(C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\eta^2\text{-C}_6\text{H}_5)_2\}\{\text{P}(\text{Me})(\text{C}_{15}\text{H}_{23})\}\text{Cl}]\cdot \text{C}_6\text{D}_6$ (at 100 K), and orthorhombic $[\text{Pt}\{\eta^2\text{-(C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)\text{P}(\eta^2\text{-C}_6\text{H}_5)_2\}\{\text{P}(\text{H})(\text{C}_{15}\text{H}_{23})\}\text{Cl}](\text{BPh}_4) \cdot \text{CH}_2\text{Cl}_2$ (at 208 K) (Scriban et al., 2006), orthorhombic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{C}_6\text{H}_8)\text{PPh}_2\}\{\text{P}(\text{Me})\text{Ph}_2\}\text{Cl}]\text{PF}_6$ (Gugger et al., 1993), and triclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{C}_2\text{B}_9\text{H}_{10})\text{PPh}_2\}(\text{PPh}_3)_2\text{Cl}]\cdot 2\text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Zhang et al., 2006), in which each chelating P^1, P^2 donor ligand creates five-membered metallocyclic ring with the mean value of $\text{P}^1\text{--Pt--P}^2$ bite angle of $86.2(\pm 0.9)^\circ$ ($\text{P}^1\text{C}_2\text{P}^2$). The values of the remaining L--Pt--L bond angles open in the sequence (mean values): $87.5(\pm 2.7)^\circ$ ($\text{P}^1\text{--Pt--Cl}$) < $92.4(\pm 3.0)^\circ$ ($\text{P}^3\text{--Pt--Cl}$) < $94.3(\pm 4.7)^\circ$ ($\text{P}^2\text{--Pt--P}^3$) < $172.9(\pm 6.8)^\circ$ ($\text{P}^1\text{--Pt--P}^3$) < $173.2(\pm 1.5)^\circ$ ($\text{P}^2\text{--Pt--Cl}$). The Pt--L bond distance elongate in the sequence (mean values): $2.230(\pm 0.023)$ Å (Pt--P^2 , trans to Cl) < $2.286(\pm 0.017)$ Å (Pt--P^1) < $2.345(\pm 0.032)$ Å (Pt--P^3) < $2.360(\pm 0.015)$ Å (Pt--Cl).

In monoclinic $[\text{Pt}\{\eta^2\text{-Me}_2\text{P}(\text{OB}(\text{F}_2)\text{O})\text{PMe}_2\}(\text{PEt}_3)_2\text{Cl}]$ (Roundhill and Roundhill, 1982) a distorted square-planar geometry about $\text{Pt}(\text{II})$ atom is build up by chelating P^1, P^2 donor ligand, monodentate PEt_3 and Cl atom. The chelating ligand creates six-membered metallocyclic ring with the value of $\text{P}^1\text{--Pt--P}^2$ bite angle of 92.4° (P^1OBOP^2). The values of the remaining L--Pt--L bond angles are: 94.4° ($\text{P}^2\text{--Pt--P}^3$), $86.6(\pm 0.8)^\circ$ ($\text{P}^1\text{--Pt--Cl}$; $\text{P}^3\text{--Pt--Cl}$), 172.5° ($\text{P}^1\text{--Pt--P}^3$), and 178.6° ($\text{P}^2\text{--Pt--Cl}$). The Pt--L bond distance elongate in the sequence: $2.194(5)$ Å (Pt--P^2 , trans to Cl) < $2.263(6)$ Å (Pt--P^1) < $2.338(6)$ Å (Pt--Cl) < $2.340(6)$ Å (Pt--P^3).

In another monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{20}\text{H}_{12})\text{PPh}_2\}(\text{PMe}_3)\text{Cl}]\text{BF}_4$ (Campbell and Gagne, 2007), the chelating- P^1, P^2 -donor ligand creates seven-membered metallocycle ring with $\text{P}^1\text{-Pt-P}^2$ bite angle of 92.3° ($\text{P}^1\text{C}_4\text{P}^2$). The remaining L-Pt-L bond angles open in the sequence: 87.5° ($\text{P}^3\text{-Pt-Cl}$) $<$ 88.9° ($\text{P}^1\text{-Pt-Cl}$) $<$ 97.8° ($\text{P}^2\text{-Pt-P}^3$) $<$ 161.0° ($\text{P}^1\text{-Pt-P}^3$) $<$ 164.4° ($\text{P}^2\text{-Pt-Cl}$). The Pt-L bond distance elongate in the sequence: $2.245 \text{ \AA}$ (Pt-P^2 , trans to Cl) $<$ $2.323 \text{ \AA}$ (Pt-P^3) $<$ $2.359 \text{ \AA}$ (Pt-Cl).

There are seven examples: monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}\text{Cl}]$ $[\text{Sn}(\text{Ph})_2\text{Cl}_4]$ and triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}\text{Cl}][\text{SnPh}_2\text{Cl}_3]$ (Garcia-Seijo et al., 2001), monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}\text{Cl}](\text{CuCl}_2)$ (Fernandez et al., 2005), monoclinic $[\text{Pt}\{\eta^3\text{-(cy-hexyl)}_2\text{P}(\text{CH}_2)_2\text{P}\{(\text{CH}_2\text{CH}_2\text{P}(\text{=O})(\text{cy-hexyl})_2(\text{CH}_2)_2\text{P}(\text{cy-hexyl})_2\}\text{Cl}\} \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (Reickborn et al., 2009), monoclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_6\text{H}_4)_2\text{P}(\text{C}_6\text{H}_4)_2\text{P}(\text{Pr}^i)_2\}\text{Cl}]$ (at 100 K) (Mazzeo et al., 2011), and monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{26}\text{H}_{23}\text{OP})\text{P}(\text{Ph})(\text{CH}_{26}\text{H}_{23}\text{OP})\text{PPh}_2\}\text{Cl}]\text{PF}_6 \cdot 4\text{MeOH}$ (at 160 K) (Clegg and Elsegood, 2017) in which each tridentate ligand creates a pair of five-membered metallocycles ($\text{P}^1\text{C}_2\text{P}^2\text{C}_2\text{P}^3$); with common P^2 atom. The mean value of the ($\text{P}^1\text{-Pt-P}^2/\text{P}^2\text{-Pt-P}^3$) bite angles is $85.4(\pm 1.5)^\circ$. The remaining L-Pt-L bond angles open in the sequence (mean values): $93.9(\pm 1.3)^\circ$ ($\text{P}^1\text{-Pt-Cl}$) $<$ $95.1(\pm 0.8)^\circ$ ($\text{P}^3\text{-Pt-Cl}$) $<$ $167.2(\pm 2.3)^\circ$ ($\text{P}^1\text{-Pt-P}^3$) $<$ $176.0(\pm 1.7)^\circ$ ($\text{P}^2\text{-Pt-Cl}$). The Pt-L bond distance elongate in the order (mean values): $2.210(\pm 0.002) \text{ \AA}$ (Pt-P^2 , trans to Cl) $<$ $2.310(\pm 0.009) \text{ \AA}$ (Pt-P^1) $\sim 2.310(\pm 0.011) \text{ \AA}$ (Pt-P^3) $<$ $2.357(\pm 0.008) \text{ \AA}$ (Pt-Cl).

In orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{P}(\text{Ph})(\text{CH}_2)_3\text{PPh}_2\}\text{Cl}]\text{ClO}_4$ (at 145 K) (Klint et al., 2004) and triclinic $[\text{Pt}\{\eta^3\text{-Pr}^i_2\text{P}(\text{C}_{11}\text{H}_8)_2\text{P}(\text{Pr}^i)(\text{C}_{11}\text{H}_8)_2\text{PP}^i_2\}\text{Cl}]\text{Cl} \cdot \text{CH}_2\text{Cl}_2$ (Ray et al., 2013), tridentate $\text{P}^1, \text{P}^2, \text{P}^3$ donor ligand creates a pair of six-membered metallocyclic rings with common P^2 atom and Cl completed a distorted square-planar geometry about Pt(II) atom. The mean values of $\text{P}^1\text{-Pt-P}^2/\text{P}^2\text{-Pt-P}^3$ bite angles is $92.5(\pm 0.9)^\circ$ ($\text{P}^1\text{C}_3\text{P}^2\text{C}_3\text{P}^3$). The remaining L-Pt-L bond angles open in the sequence: 86.8° ($\text{P}^3\text{-Pt-Cl}$) $<$ 88.0° ($\text{P}^1\text{-Pt-Cl}$) $<$ 171.6° ($\text{P}^1\text{-Pt-P}^3$) $<$ 179.4° ($\text{P}^2\text{-Pt-Cl}$). The Pt-L bond distance elongate in the sequence: $2.239 \text{ \AA}$ (Pt-P^2 , trans to Cl) $<$ $2.302 \text{ \AA}$ (Pt-P^1) $<$ $2.313 \text{ \AA}$ (Pt-P^3) $<$ $2.365 \text{ \AA}$ (Pt-Cl).

In monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)_2(\text{C}_6\text{H}_4)_2\text{N}_2\text{P}(\text{Cl})(\text{C}_6\text{H}_4)_2\text{PPh}_2\}\text{Cl}]\text{PF}_6$ (at 120 K) (Day et al., 2011), and monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)_2\{\text{N}(\text{CH}_2)_2\text{N}\}\text{P}(\text{C}_6\text{H}_4)_2\text{PPh}_2\}\text{Cl}]\text{PF}_6$ (at 120 K) (Pan et al., 2012a), tridentate $\text{P}^1, \text{P}^2, \text{P}^3$ -donor ligand creates a pair of six-membered metallocyclic rings with common P^2 atom ($\text{P}^1\text{C}_2\text{NP}^2\text{NC}_2\text{P}^3$) with Cl build up a distorted square-planar geometry about Pt(II) atom. The mean value of $\text{P}^1\text{C}_2\text{NP}^2/\text{P}^2\text{NC}_2\text{P}^3$ bite angles is $89.2(\pm 1.6)^\circ$.

The remaining L-Pt-L bond angles open in the sequence: 88.6° ($\text{P}^3\text{-Pt-Cl}$) $<$ 92.7° ($\text{P}^1\text{-Pt-Cl}$) $<$ 174.7° ($\text{P}^1\text{-Pt-P}^3$) $<$ 179.4° ($\text{P}^2\text{-Pt-Cl}$). The bond distance elongate in the sequence: $2.155 \text{ \AA}$ (Pt-P^2 , trans to Cl) $<$ $2.298 \text{ \AA}$ (Pt-P^1) $<$ $2.302 \text{ \AA}$ (Pt-P^3) $<$ $2.334 \text{ \AA}$ (Pt-Cl).

2.6 PtP_3S type

There are seven examples of this type. In yellow triclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}\{\eta^2\text{-Ph}_2\text{PN}(\text{Et})\text{C}(\text{NEt})\text{S}\}]\text{Okeya et al., 1992}$ two bidentate donor ligands, one homo- (P^1, P^2) and another one hetero- (P^3, S) build up a distorted square-planar geometry about platinum atom. The homobidentate creates a four-membered metallocyclic ring with the value of $\text{P}^1\text{-Pt-P}^2$ bite angle of 71.4° (P^1CP^2) and hetero-creates five-membered with the value of $\text{P}^3\text{-Pt-S}$ bite angle of 85.7° (P^3NCS). The remaining L-Pt-L bond angles open in the sequence: 96.8° ($\text{P}^1\text{-Pt-S}$) $<$ 108.6° ($\text{P}^2\text{-Pt-P}^3$) $<$ 164.8° ($\text{P}^2\text{-Pt-S}$) $<$ 177.20° ($\text{P}^1\text{-Pt-P}^3$). The Pt-L bond distance elongate in the sequence: $2.269 \text{ \AA}$ (Pt-P^2 , trans to S) $<$ $2.291 \text{ \AA}$ (Pt-S) $<$ $2.303 \text{ \AA}$ (Pt-P^1) $<$ $2.309 \text{ \AA}$ (Pt-P^3).

In yellow three monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}\{\eta^1\text{-Et}_2\text{NCS}_2\}]\text{Colton et al., 1993}$, monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}(\text{SPh})]\text{CF}_3\text{SO}_3$, $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}(\text{SC}_6\text{HF}_4)]\text{CF}_3\text{SO}_3$, and triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}(\text{SC}_6\text{F}_4(\text{CF}_3))]\text{CF}_3\text{SO}_3$ (Cervantes et al., 2015), each tridentate $\text{-P}^1, \text{P}^2, \text{P}^3\text{-}$ donor ligand creates a pair of five-membered metallocycles with common P^2 atom ($\text{P}^1\text{C}_2\text{P}^2\text{C}_2\text{P}^3$) with the mean value of $\text{P}^1\text{-Pt-P}^2/\text{P}^2\text{-Pt-P}^3$ bite angles of $85.0(\pm 0.6)^\circ$. The mean value of cis-P-Pt-S bond angles is $92.7(\pm 3.1)^\circ$. The Pt-L bond distance elongate in sequence: $2.233 \text{ \AA}$ (Pt-P^2 , trans to S) $<$ $2.287 \text{ \AA}$ (Pt-P^1) $<$ $2.396 \text{ \AA}$ (Pt-S).

In triclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)_2\text{S}(\text{=O})(\text{C}_6\text{H}_4)_2\text{PPh}_2\}(\text{PPh}_3)] \cdot 0.5\text{CH}_2\text{Cl}_2$ (at 100 K) (Figure 6) (Suess and Peters, 2012) and orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2\}(\text{PPh}_3)](\text{ClO}_4)_2 \cdot \text{Me}_2\text{CO}$ (at 120 K) (Andreasen et al., 2002), tridentate $\text{-P}^1\text{-S}^1\text{-P}^2\text{-}$ donor ligand creates a pair of five-membered metallocycles with common S^1 atom ($\text{P}^1\text{C}_2\text{S}^1\text{C}_2\text{P}^2$). The mean value of $\text{P}^1\text{C}_2\text{S}^1/\text{S}^1\text{C}_2\text{P}^2$ bite angles is $89.0(\pm 0.3)^\circ$. The Pt-L bond distance elongate in the sequence: $2.271 \text{ \AA}$ (Pt-P^1) $<$ $2.276 \text{ \AA}$ (Pt-P^2) $<$ $2.281 \text{ \AA}$ (Pt-P^3 , trans to S) $<$ $2.313 \text{ \AA}$ (Pt-S).

2.7 PtP_3Br type

Yellow triclinic $[\text{Pt}\{\eta^2\text{-Bu}^t\text{PP}=\text{P}(\text{Bu}^t)_2\}(\text{PPh}_3)]\text{Br}$ (at 243 K) (Figure 7) (Kovacs et al., 1997) is only example of this type. The chelating $\text{-P}^1, \text{P}^2\text{-}$ donor ligand with P^3Ph_3 and Br

Figure 6: Structure of $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(\text{=O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{PPh}_3)]$ (Suess and Peters, 2012).

Figure 7: Structure of $[\text{Pt}\{\eta^2\text{-Bu}_2\text{P=PPBu}_2\}(\text{PPh}_3)\text{Br}]$ (Kovacs et al., 1997).

anion build up a distorted square-planar geometry about Pt atom. The chelating ligand forms three membered metallocycle with the value of $\text{P}^1\text{-Pt-P}^2$ bite angle of 55.1° (P^1P^2). The Pt-L bond distance elongate in the sequence: $2.231 \text{ \AA}$ (Pt-P^1 , trans to Br) $< 2.297 \text{ \AA}$ (Pt-P^2) $< 2.405 \text{ \AA}$ (Pt-P^3) $< 2.410 \text{ \AA}$ (Pt-Br). The mean value of cis-P-Pt-Br bond angles is $96.1(\pm 5.3)^\circ$.

2.8 PtP_3I type

There are three examples of this type. In yellow orthorhombic $[\text{Pt}\{\eta^2\text{-(}\eta^2\text{-C}_6\text{H}_{12}\text{)P}(\text{C}_6\text{H}_4\text{)P}(\eta^2\text{-C}_6\text{H}_{12}\text{))}\{\text{P}(\text{Me})(\text{C}_{15}\text{H}_{23})\}\text{I}]$ (at 203 K) (Scriban et al., 2006) the chelating

Figure 8: Structure of $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\{\text{N}(\text{CH}_2)_2\text{N}\}\text{P}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}]\text{I}^+$ (Pan et al., 2012b).

$\text{-P}^1, \text{P}^2$ donor ligand creates five-membered metallocyclic ring with value of $\text{P}^1\text{-Pt-P}^2$ bite angle of 86.1° ($\text{P}^1\text{C}_2\text{P}^2$). The Pt-L bond distance elongate in the sequence: $2.231 \text{ \AA}$ (Pt-P^2 , trans to I) $< 2.291 \text{ \AA}$ (Pt-P^1) $< 2.393 \text{ \AA}$ (Pt-P^3) $< 2.640 \text{ \AA}$ (Pt-I). The value of cis- $\text{P}^2\text{-Pt-P}^3$ bond angle is 94.9° , trans- $\text{P}^1\text{-Pt-P}^3$ bond angle is 169.0° and trans- $\text{P}^2\text{-Pt-I}$ is 172.0° .

In orthorhombic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{CH}_2)_2\text{PPh}_2\}\text{I}]\cdot 0.2\text{CHCl}_3\cdot 0.5\text{H}_2\text{O}$ (at 220 K) (Parsons et al., 2004) tridentate $\text{-P}^1, \text{P}^2, \text{P}^3$ donor ligand creates a pair of five-membered metallocyclic rings with the common P^2 atom ($\text{P}^1\text{C}_2\text{P}^2\text{C}_2\text{P}^3$) with the value of $\text{P}^1\text{-Pt-P}^2/\text{P}^2\text{-Pt-P}^3$ bite angle of 84.9° . The values of Pt-L bond distances are: $2.249 \text{ \AA}$ (P^2 , trans to I) $< 2.309 \text{ \AA}$ (P^1, P^3) and $2.64 \text{ \AA}$ (I).

In monoclinic $[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\{\text{N}(\text{CH}_2)_2\text{N}\}\text{P}(\text{Me})(\text{C}_6\text{H}_4)\text{PPh}_2\}]\text{PF}_6\cdot \text{CH}_2\text{Cl}_2$ (at 120 K) (Figure 8) (Pan et al., 2012b). As can be seen the tridentate $\text{-P}^1, \text{P}^2, \text{P}^3$ -donor ligand creates a pair of six-membered metallocyclic rings with the common P^2 atom ($\text{P}^1\text{C}_2\text{NP}^2\text{NC}_2\text{P}^3$). The mean value of $\text{P}^1\text{-Pt-P}^2/\text{P}^2\text{-Pt-P}^3$ bite angles is $87.2(\pm 2.1)^\circ$. The values of remaining L-Pt-L bond angles are: 92.8° ($\text{P}^1\text{-Pt-I}$), 173.5° ($\text{P}^1\text{-Pt-P}^3$), and 175.0° ($\text{P}^2\text{-Pt-I}$). The Pt-L bond distance elongate in the sequence: $2.227 \text{ \AA}$ (Pt-P^2 , trans to I) $< 2.312 \text{ \AA}$ (Pt-P^3) $< 2.322 \text{ \AA}$ (Pt-P^1) $< 2.638 \text{ \AA}$ (Pt-I).

3 Conclusions

This review includes over fifty monomeric Pt(II) coordination complexes with composition of PtP_3X ($\text{X} = \text{H}$, OL, NL, BL, Cl, SL, Br, or I). These complexes crystallized in three crystal classes: monoclinic (23 examples),

triclinic (17 examples), and orthorhombic (11 examples). On the basis of variable combination of donor ligands which build up PtP₃X, can be divided into the five sub-groups.

To each sub-group the bond distance (mean values) with sums of Pt–L(x4) bond distances are:

I. Pt(η²-P¹,P²L)(P³L)X:

PtP₃H: 2.253 Å (Pt–P¹); 2.326 Å (Pt–P², trans to H); 2.310 Å (Pt–P³); 1.65 Å (Pt–H); Σ 8.54 Å (Campbell and Gagne, 2007; Charles et al., 1996; Jaska et al., 2003, 2005; Kovacik et al., 2000).

PtP₃Cl: 2.290 Å (Pt–P¹); 2.226 Å (Pt–P², trans to Cl); 2.334 Å (Pt–P³); 2.357 Å (Pt–Cl); Σ 9.21 Å (Bader et al., 1992, 1995; Bhattacharyya et al., 1993; Caliman, 1998; Campbell and Gagne, 2007; Gomez-Ruiz et al., 2007; Gugger et al., 1993; Hu et al., 2009; Khasnis et al., 1992; Roundhill and Roundhill 1982; Scriban et al., 2006; Zhang et al., 2006).

PtP₃Br: 2.291 Å (Pt–P¹); 2.231 Å (Pt–P², trans to Br); 2.405 Å (Pt–P³); 2.510 Å (Pt–Br); Σ 9.44 Å (Kovacs et al., 1997).

PtP₃I: 2.290 Å (Pt–P¹); 2.300 Å (Pt–P², trans to I); 2.393 Å (Pt–P³); 2.640 Å (Pt–I); Σ 9.56 Å (Scriban et al., 2006).

II. Pt(η²-P¹,P²L)(η²-P³,X):

PtP₃N: 2.324 Å (Pt–P¹); 2.271 Å (Pt–P², trans to N); 2.340 Å (Pt–P³); 2.079 Å (Pt–N); Σ 9.01 Å. (Lenero et al., 2013; Zhang et al., 2011).

PtP₃S: 2.309 Å (Pt–P¹); 2.303 Å (Pt–P², trans to S); 2.269 Å (Pt–P³); 2.291 Å (Pt–S); Σ 9.17 Å (Okeya et al., 1992).

III. Pt(η³-P¹,P²,P³L)X:

PtP₃O: 2.322 Å (Pt–P¹); 2.196 Å (Pt–P², trans to O); 2.315 Å (Pt–P³); 2.109 Å (Pt–O); Σ 8.94 Å (Annibale et al., 2000; Fernandez et al., 2001).

PtP₃Cl: 2.300 Å (Pt–P¹); 2.197 Å (Pt–P², trans to Cl); 2.307 Å (Pt–P³); 2.349 Å (Pt–Cl); Σ 9.15 Å (Clegg and Elsegood, 2017; Day et al., 2011; Fernandez et al., 2005; Klint et al., 2004; Mazzeo et al., 2011; Pan et al., 2012a; Ray et al., 2013; Reickborn et al., 2009).

PtP₃S: 2.292 Å (Pt–P¹); 2.233 Å (Pt–P², trans to S); 2.293 Å (Pt–P³); 2.393 Å (Pt–S); Σ 9.21 Å (Cervantes et al., 2015; Colton et al., 1993).

PtP₃I: 2.312 Å (Pt–P¹); 2.227 Å (Pt–P², trans to I); 2.322 Å (Pt–P³); 2.638 Å (Pt–I); Σ 9.50 Å (Pan et al., 2012b; Parsons et al., 2004).

IV. Pt(η³-P¹,X¹,P²)(P³L):

PtP₃O¹: 2.297 Å (Pt–P¹); 2.312 Å (Pt–P²); 2.239 Å (Pt–P³, trans to O); 2.189 Å (Pt–O); Σ 9.04 Å (Lenero et al., 2013).

PtP₃N¹: 2.309 Å (Pt–P¹); 2.325 Å (Pt–P²); 2.270 Å (Pt–P³, trans to N); 2.082 Å (Pt–N); Σ 8.98 Å (Takeuchi et al., 2016).

PtP₃S¹: 2.271 Å (Pt–P¹); 2.276 Å (Pt–P²); 2.281 Å (Pt–P³, trans to S); 2.313 Å (Pt–S); Σ 9.14 Å (Andreasen et al., 2002; Suess and Peters, 2012).

V. Pt(η²-P¹, BL)(PPH₃)₂:

PP₃B: 2.310 Å (Pt–P¹); 2.354 Å (Pt–P², trans to B); 2.340 Å (Pt–P³); 2.262 Å (Pt–B); Σ 9.27 Å (Amgoune et al., 2012).

The Pt–P (rans to X) bond distance elongate in the sequence (total mean values): 2.212 Å (X=Cl) < 2.218 Å (OL) < 2.231 Å (Br) < 2.264 Å (I) < 2.270 Å (NL) < 2.272 Å (SL) < 2.326 Å (H); which corresponds quite well with trans influence of the respective X- donor atoms. The total mean values of Pt–P (bis and tridentate) and Pt–PR₃ (monodentate) bond distances (mutually trans) are: 2.288 and 2.326 Å. The Pt–X (trans to P) bond distance elongate in the sequence (total mean values): 1.65 Å (X=H) < 2.086 Å (NL) < 2.150 Å (OL) < 2.262 Å (BL) < 2.332 Å (SL) < 2.353 Å (Cl) < 2.510 Å (Br) < 2.639 Å (I). The sum of Pt–L(x4) bond distances growing in the sequence: 8.54 Å (PtP₃H) < 8.97 Å (PtP₃O) < 9.00 Å (PtP₃N) < 9.17 Å (PtP₃S) < 9.19 Å (PP₃Cl) < 9.27 Å (PtP₃B) < 9.44 Å (PtP₃Br) < 9.52 Å (PtP₃I); which corresponds quite well with covalent radii of X atoms, except S and B atoms.

The chelating ligands create wide varieties of the metallocyclic rings: three- PB, PP; four- PCN, PCP, PPP; five- PC₂N, PC₂O, PC₂P, PC₂S; six- PC₃P, POBOP; seven- PC₄P; and eight-PC₂OC₂P, membered. There are at least two contributing factors to the size of chelate bond angles both ligand based. One is the steric constraints imposed on the ligand and the other is the need to accommodate bidenticity there appropriate. The L–Pt–L chelate bond angles open in the sequence (mean values): 49.6° (PB) < 55.1° (PP) < 69.1° (PCN) < 71.2° (PCP) < 78.2° (PPP) < 81.0° (PC₂N) < 81.7° (PC₂O) < 86.3° (PC₂P) < 89.0° (PC₂S) < 92.4° (POBOP) < 92.5° (PC₃P) < 94.4° (PC₂OC₂P) < 95.1° (PC₄P).

In transition metal complexes, the oxidation state 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 molecule shape and degree of distortion as well as exemplified best the τ₄ parameter for a square-planar geometry by equation introduced by (Yang et al., 2007):

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141} \text{ for tetrahedral, and} \quad (1)$$

$$\tau_4 = \frac{360 - (\alpha + \beta)}{360} \text{ for square planar}$$

The values of τ_4 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 τ_4 for the respective complexes with the PtP_3X chromophores, growing in the sequence: $0.040 (\text{PtP}_3\text{H}) < 0.042 (\text{PtP}_3\text{I}) < 0.045 (\text{PtP}_3\text{Br}) < 0.049 (\text{PtP}_3\text{Cl}) < 0.050 (\text{PtP}_3\text{S}) < 0.056 (\text{PtP}_3\text{O}) < 0.065 (\text{PtP}_3\text{N}) < 0.15 (\text{PtP}_3\text{B})$. The distortion of the square-planar geometry increases in the given sequence there is a cooperative effect between a degree of distortion and trans influence o X atom/ligand, when trans-influence of the respective X weakness degree of distortion increases.

During the collection and organization of the data has become evident that some original papers are lacking important information such as atom coordinates and analysis of intermolecular distances. In view of these limitations we believe that such review as this can continue to serve a useful function by centralizing available material and delineating areas worthy of further investigation.

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