Research Article

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Organodiphosphines in PtP_2X_2 (X = As, Ge or Te) derivatives – Structural aspects

<https://doi.org/10.1515/mgmc-2020-0016>

Received July 01, 2020; accepted July 16, 2020.

Abstract: Structural data of $\text{cis-Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ (X = Ge or Te), $\text{cis-Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = As, Ge or Te) and $\text{trans-Pt}(\eta^2\text{-P}_2\text{L})_2$ were classified and analyzed. The chelating ligands create varieties of metallocyclic rings, which open in the sequence: 83.1° (GeGeGe) < 83.8° (AsC₂As) < 86.2° (PC₂P) < 88.5° (PC₂Te) < 89.7° (PC₃P) ~ 89.7° (GeGeGe). The structural data are compared and discussed with the complexes of an inner coordination spheres $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ (X = O, N, CN, B, Cl, S, Se, Si, Br or I), $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = O, N, S, Se or Si), and $\text{Pt}(\eta^2\text{-P}_2\text{SiL})_2$.

Keywords: organodiphosphines; PtP_2X_2 (X = As, Ge, Te); structures; review; trans-influence

$\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$	1,2-bis(dimethylphosphino)ethane
$(\text{Ph})(\text{Me})\text{As}(\text{CH}_2)_2\text{As}(\text{Me})(\text{Ph})$	bis(phosphylmethylarsene)ethane-1,2-diyl
$(\text{Ph})(\text{Me})\text{P}(\text{C}_6\text{H}_4)\text{P}(\text{M})(\text{Ph})$	bis(phenylmethylphosphino)phenylene-1,2-diyl
$\text{Ph}_2\text{P}(\text{C}_{10}\text{H}_6)\text{PPh}_2$	naphtalene-1,8-diyl bis(diphenylphosphine)
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	1,2-bis(diphenylphosphino)ethane
$\text{Te}(\text{C}_4\text{H}_3\text{S})$	2-thienyltellurate
$\text{Te}(\text{C}_5\text{H}_8\text{O})\text{Te}$	oxetane-3,3-diyl dimethanetellurate
$\text{Te}(\text{mes})_3$	2,4,6-trimethylbenzenetellurate
TePh	phenyltellurate

Abbreviations:

$(\text{GePh}_2)_3$	1,1,2,2,3,3-hexaphenyl-trigerman-1,3-diyl
$\text{Ge}(\text{H})(\text{Bu}^n)_2$	di-n-butylgermyl
$\text{Ge}(\text{H})(\eta^2\text{-(C}_{12}\text{H}_8)$	(biphenyl-2,2'-diyl)hydridogermyl
$\text{Ge}(\text{H})_2(\text{C}_{12}\text{H}_{17})$	2,4,6-triethylphenylgermyl
$\text{Ge}(\text{Me})(\text{Ph})_2$	methyl(diphenylgermyl
$\text{Ge}(\text{mes})_3$	tri(mesitylgermyl
$\text{Ge}(\text{Ph})_2$	di(phenylgermyl

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1 Introduction

Comprehensive view on structural parameters of almost 2000 monomeric platinum complexes shows, that the square-planar Pt(II) complexes, by far prevail (Holloway and Melnik, 2002, 2003, 2004). One of such interest of a square-planar Pt(II) complexes is anti-tumor activity of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, known as “cisplatin” (Rosenberg et al., 1969). Over 200 platinum complexes exist in isomeric forms, which were classified and analyzed (Melník and Holloway, 2006), included are distortion (65%), cis-trans (30%), mixed (cis-trans + distortion) isomers, and ligand isomerization.

There are numerous published structural studies of organomonophosphines platinum complexes, which were classified and analyzed (Melník and Mikuš, 2015). There are also numerous structures of Pt(II) complexes with organomonophosphines (Holloway and Melnik, 2002, 2003, 2004; Melník and Mikuš 2019a, 2019b, 2020; Melník et al., 2019). The aim of this review is to classified and analyzed structural parameters of $\text{cis-Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ (X = Ge, Te), $\text{cis-Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = As, Ge, Te) and $\text{trans-Pt}(\eta^2\text{-P}_2\text{L})_2$. Their structural data are compared

and discussed with $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ ($\text{X} = \text{O}, \text{N}, \text{CN}, \text{B}, \text{Cl}, \text{S}, \text{Br}, \text{Se}, \text{Si}, \text{I}$), $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ ($\text{X} = \text{O}, \text{N}, \text{S}, \text{Se}, \text{Si}$) and $\text{Pt}(\eta^2\text{-P}_2\text{SiL})_2$ complexes.

2 Cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-As}_2\text{L})$ derivative

Orthorhombic $\text{cis-}[\text{Pt}\{\eta^2\text{-(Ph)(Me)P(C}_6\text{H}_4\text{)P(Me)(Ph)}\}\{\eta^2\text{-(Ph)(Me)As(CH}_2\text{)}_2\text{As(Me)(Ph)}\}]. 2\text{CF}_3\text{SO}_3$ (at 200K) (Weir et al., 2009), is only example of such type (Figure 1). As can be seen both homobidentate ligands create five-membered metallocyclic rings with the values of L-Pt-L bite angles of $86.8(2)^\circ$ (PC_2P) and $83.8(2)^\circ$ (AsC_2As). The mean values of cis- and trans- P-Pt-As bond angles are $95.2(\pm 0.2)$ and $172.2(\pm 0.1)^\circ$, respectively. The mean values of Pt-L bond distances are $2.276(\pm 5)$ ($\text{L} = \text{P}$) and $2.422(\pm 8)$ Å (As), respectively.

3 Cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})\text{Ge}_2$ derivatives

There are ten examples of the such inner coordination sphere about the Pt(II) atoms. These complexes from a coordination mode of the respective donor ligands can be divided into to the two sub-groups $\text{Pt}(\eta^2\text{-P}_2\text{L})\text{GeL}_2$ and $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-Ge}_2\text{L})$.

3.1 Cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{GeL})_2$ derivatives

There are seven complexes of this type of the inner coordination sphere about Pt(II) atom. In five complexes:

Figure 1: Structure of $\text{cis-}[\text{Pt}\{\eta^2\text{-(Ph)(Me)P(C}_6\text{H}_4\text{)P(Me)(Ph)}\}\{\eta^2\text{-(Ph)(Me)As(CH}_2\text{)}_2\text{As(Me)(Ph)}\}]. 2\text{CF}_3\text{SO}_3$ (Weir et al., 2009).

monoclinic $[\text{Pt}\{\eta^2\text{-Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2\}\{\text{Ge(Me)(Ph)}_2\}_2]$ and monoclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\}\{\text{Ge(Me)(Ph)}_2\}_2] \cdot \text{C}_6\text{H}_6$ (Mochida et al., 2001), orthorhombic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\}\{\text{Ge(mes)}_2\}_2]$ (at 120 K) and monoclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\}\{\text{Ge(H)(}\eta^2\text{-C}_{12}\text{H}_8\text{)}_2\}_2]$ (at 120 K) (Arii et al., 2012), tetragonal $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\}\{\text{Ge(H)(}\eta^2\text{-C}_{12}\text{H}_8\text{)}_2\}_2]$ (at 100 K) (Braddock-Wilking et al., 2009), and monoclinic $[\text{Pt}\{\eta^2\text{-Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2\}\{\text{Ge(H)(Bu}^n\text{)}_2\}_2]$ (at 113 K) (Tanabe et al., 2011), each $\text{R}_2\text{P(CH}_2\text{)}_2\text{PR}_2$ ligand creates five-membered metallocyclic ring (PC_2P) with the mean value of P-Pt-P bite angles of $85.6(\pm 1.0)^\circ$. The mean value of Ge-Pt-Ge bond angles is $85.6(\pm 2.6)^\circ$ and the mean values of cis- and trans- P-Pt-Ge bond angles are $94.5(\pm 3.6)^\circ$ and $174.2(\pm 5.0)^\circ$, respectively. The mean values of Pt-P and Pt-Ge bond distance are $2.286(\pm 2)$ and $2.471(\pm 14)$ Å, respectively. In triclinic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P(CH}_2\text{)}_3\text{PPh}_2\}\{\text{Ge(mes)}_2\}_2] \cdot 0.75\text{hexane} \cdot 1.58\text{toluene}$ (Arii et al., 2012) the chelating ligand creates six-membered metallocyclic rings (PC_3P) with the value of P-Pt-P bite angle of 95.8° . The Ge-Pt-Ge bond angle is 81.4° . The mean Pt-L bond distances are 2.282 Å ($\text{L}=\text{P}$) and 2.471 Å (Ge) respectively.

3.2 Cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-Ge}_2\text{L})$ derivatives

In monoclinic $[\text{Pt}\{\eta^2\text{-Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2\}\{\eta^2\text{-(GePh}_2\text{)}_3\}_2]$ (Figure 2) (Tanabe et al., 2009), two dissimilar chelating ligands build up a distorted square-planar environments

Figure 2: Structure of $[\text{Pt}\{\eta^2\text{-Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2\}\{\eta^2\text{-(GePh}_2\text{)}_3\}_2]$ (Tanabe et al., 2009).

(PtP₂Ge₂). The P,P-donor ligand creates five-membered metalocycle (PC₂P) with the P–Pt–P angle of 85.9°, and (GePh₂)₃ ligand form four-membered metalocycle (GeGeGe) with the value of Ge–Pt–Ge angle of 83.1°. The mean values of cis- and trans-P–Pt–Ge bond angles are 95.7(±1.0) and 174.9(±0.4)°, respectively. The mean values of Pt–P and Pt–Ge bond distances are 2.280(±2) and 2.452(±22) Å, respectively.

There are two complexes monoclinic [Pt{η²-Ph₂P(CH₂)₂PPh₂}{η²-(Ge(η²-C₁₂H₈))₄}]·CH₂Cl₂ (at 100 K) (Braddock-Wilking et al., 2009) and orthorhombic [Pt{η²-Me₂P(CH₂)₂PMe₂}{η²-(Ge(Ph₂)₄)}]·toluene (at 113 K) (Tanabe et al., 2009) each R₂P(CH₂)₂PR₂ creates five-membered metalocycles with the mean value of P–Pt–P bite angle of 85.7° (PC₂P). Each bidentate Ge,Ge'-donor ligand forms five-membered metalocyclic ring with the mean Ge–Pt–Ge bite angle of 89.7° (GeGe₂Ge). The mean values of cis- and trans-P–Pt–Ge bond angles are 92.4(±1.4) and 175.1(±1.1)°, respectively. The mean values of Pt–L bond distances are 2.285 Å (L = P) and 2.464 Å (Ge), respectively.

4 Cis-Pt(η²-P₂L)Te₂ derivatives

There are seven examples of the such inner coordination sphere about the Pt(II) atom. These complexes from a coordination mode of the respective donor ligands can be divided into the three sub-groups: Pt(η²-P₂L)(TeL)₂, Pt(η²-P₂L)(η²-Te₂L), and Pt(η²-P₂TeL)₂.

4.1 Cis-Pt(η²-P₂L)(TeL)₂ derivatives

In five complexes a distorted square-planar geometry about the Pt(II) atom is build up by bidentate P,P'-donor ligand with pair of monodentate Te donor ligands. In two monoclinic [Pt{η²-Ph₂P(CH₂)₂PPh₂}(TePh)₂] (at 120 K) and [Pt{η²-Ph₂P(CH₂)₂PPh₂}(Te(C₄H₃S))₂] (at 120 K) (Risto et al., 2007) each Ph₂P(CH₂)₂PPh₂ forms a five-membered metalocyclic ring with the mean value of 86.6° (PC₂P). In another three complexes: orthorhombic [Pt{η²-Ph₂P(CH₂)₃PPh₂}(Te(mes))₂]-3C₆H₆ (at 100 K) (Chauhan et al., 2013), monoclinic [Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(Te(Ph))₂]-3toluene (at 133 K), and triclinic [Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(Te(C₄H₃S))₂] (at 133 K) (Karjalainen et al., 2017) each of the bidentate-P,P-donor ligand creates six-membered metalocyclic ring with the mean value of P–Pt–P bite angle of 91.2° (PC₃P). Structure of [Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(Te(C₄H₃S))₂] (Karjalainen et al., 2017)

is shown in Figure 3 as an example. The total mean values of Pt–L bond distances are 2.261 Å (L = P) and 2.585 Å (Te).

4.2 Cis-Pt(η²-P₂L)(η²-Te₂L) derivative

In monoclinic cis-[Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(η²-Te(C₅H₈O)Te)] (at 120 K) (Figure 4) (Wagner et al., 2008) two chelating ligands, one with P,P-donor atoms and the other one with Te,Te-donor atom create a distorted square-planar

Figure 3: Structure of [Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(Te(C₄H₃S))₂] (Karjalainen et al., 2017).

Figure 4: Structure of cis-[Pt{η²-Ph₂P(C₁₀H₆)PPh₂}(η²-Te(C₅H₈O)Te)] (Wagner et al., 2008).

geometry about the Pt(II) atom (PtP_2Te_2). Each chelating ligand forms six-membered metallocycles (PC_3P) and (TeC_3Te) with the values of L–Pt–L bite angles of 88.3° and 90.8° , respectively. The mean values of cis- and trans-Pt–Pt–Te bond angles are 90.6° and 175.0° , respectively. The mean values of Pt–L bond distances are $2.254 \text{ \AA}$ (P) and $2.627 \text{ \AA}$ (Te).

5 Trans- $\text{Pt}\{\eta^2\text{-P,TeL}\}_2$ derivative

Triclinic trans- $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{TePh}\}_2][\text{Pt}(\text{SCN})_4]\cdot 2\text{dmf}$ (Gysling and Luss, 1984) consists from well separated $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{TePh}\}_2]^{2+}$ (Figure 5) and $[\text{Pt}(\text{SCN})_4]^{2-}$. In the complex cation a distorted square-planar geometry about Pt(II) atom is build up by a pair of heterobidentate-P,Te donor ligands. Each heterochelating ligand creates five-membered metallocyclic ring with the mean P–Pt–Te bite angle of 88.5° (PC_2Te). The values of trans-P–Pt–P and Te–Pt–Te bond angles is 178° . The mean values of Pt–L bond distances are $2.306(1) \text{ \AA}$ (L = P) and $2.575(1) \text{ \AA}$ (Te), respectively.

6 Conclusions

This review covers structural parameters of monomeric platinum complexes with an inner coordination spheres of $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ (X = Ge, Te), $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = As, Ge, Te) and $\text{Pt}(\eta^2\text{-P,TeL})_2$. In cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{GeL})_2$ complexes the

mean values of Pt–P (trans to Ge) and Pt–Ge (trans to P) bond distances are 2.286 and $2.471 \text{ \AA}$, respectively. Such values in cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{TeL})_2$ are $2.261 \text{ \AA}$ (Pt–P) and $2.585 \text{ \AA}$ (Pt–Te), respectively. In cis- $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ complexes the mean values are: 2.276 and $2.442 \text{ \AA}$ (X = As); 2.283 and $2.456 \text{ \AA}$ (X = Ge); 2.254 and $2.627 \text{ \AA}$ (X = Te), respectively. In trans- $\text{Pt}(\eta^2\text{-P,TeL})_2$ complex the values are: $2.306 \text{ \AA}$ (P trans to P) and $2.575 \text{ \AA}$ (Te trans to Te).

The chelating donor ligands create varieties of metallocyclic rings which open in the sequence (mean values): 83.1° (GeGeGe) < 83.8° (AsC₂As) < 86.2° (PC_2P) < 88.5° (PC_2Te) < 89.7° (PC_3P) ~ 89.7° (GeGe₂Ge). The sum of four (Pt–P(x2)) + (Pt–X(x2)) bond distances $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ vs $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ are: 9.406 vs $9.481 \text{ \AA}$ (X = Ge); 9.692 vs $9.754 \text{ \AA}$ (X = Te). For $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-As}_2\text{L})$ the value is $9.396 \text{ \AA}$, and for $\text{Pt}(\eta^2\text{-P,TeL})_2$ is $9.762 \text{ \AA}$. These values indicate that the inner coordination sphere in $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ is somewhat more crowded than in its $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ partner.

This review together with its precursors (Holloway and Melník, 2002, 2003, 2004; Melník and Mikuš 2019a, 2019b, 2020; Melník et al., 2019) have summarized and analyzed structural parameters of almost four hundred monomeric platinum(II) coordination complexes with an inner coordination spheres about the Pt(II) atoms of $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ (X = OL, NL, CN, BL, Cl, SL, Br, SeL, SiL, AsL, GeL, I, or TeL); $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = O₂L, N₂L, S₂L, Se₂L, Si₂L, As₂L, Ge₂L or Te₂L); and $\text{Pt}(\eta^2\text{-P,XL})_2$ (X = Si or Te). In the $\text{Pt}(\eta^2\text{-P}_2\text{L})(\text{XL})_2$ derivatives the total mean Pt–P (trans to X) bond distance elongate in the sequence: $2.216 \text{ \AA}$ (X = O) < $2.233 \text{ \AA}$ (Br) < $2.240 \text{ \AA}$ (I) < $2.247 \text{ \AA}$ (S) < $2.249 \text{ \AA}$ (Se) < $2.260 \text{ \AA}$ (N) < $2.261 \text{ \AA}$ (Te) < $2.286 \text{ \AA}$ (Ge) < $2.290 \text{ \AA}$ (Cl) < $2.319 \text{ \AA}$ (Si) < $2.332 \text{ \AA}$ (B) < $2.335 \text{ \AA}$ (C), and the total mean Pt–X (trans to P) bond distance elongate in the sequence: $2.00 \text{ \AA}$ (X = C) < $2.045 \text{ \AA}$ (B) < $2.090 \text{ \AA}$ (O) < $2.10 \text{ \AA}$ (N) < $2.350 \text{ \AA}$ (S) < $2.356 \text{ \AA}$ (Cl) < $2.365 \text{ \AA}$ (Si) < $2.455 \text{ \AA}$ (Se) < $2.471 \text{ \AA}$ (Ge) < $2.490 \text{ \AA}$ (Br) < $2.585 \text{ \AA}$ (Te) < $2.666 \text{ \AA}$ (I). As can be seen from the respective bond distances, the “soft” donor ligands show a larger trans-influence than the “borderline” or “hard” ones. The sum of all four (Pt–P(x2)) + (Pt–X(x2)) bond distances in these complexes with cis-configuration increases quite well with the covalent radius of the respective X donor atoms in the sequence: $8.61 \text{ \AA}$ (PtP_2O_2) < $8.67 \text{ \AA}$ (PtP_2C_2) < $8.72 \text{ \AA}$ (PtP_2N_2) < $8.75 \text{ \AA}$ (PtP_2B_2) < $9.19 \text{ \AA}$ (PtP_2S_2) < $9.29 \text{ \AA}$ (PtP_2Cl_2) < $9.37 \text{ \AA}$ (PtP_2Si_2) < $9.41 \text{ \AA}$ (PtP_2Se_2)(PtP_2Ge_2) < $9.45 \text{ \AA}$ (PtP_2Br_2) < $9.69 \text{ \AA}$ (PtP_2Te_2) < $9.81 \text{ \AA}$ (PtP_2I_2).

In the $\text{Pt}(\eta^2\text{-P}_2\text{L})(\eta^2\text{-X}_2\text{L})$ (X = O₂L, N₂L, S₂L, Se₂L, Si₂L, As₂L, Ge₂L, or Te₂L) derivatives the total mean Pt–P (trans to X) bond distance elongate in the sequence: $2.215 \text{ \AA}$ (X = O) < $2.242 \text{ \AA}$ (N) < $2.254 \text{ \AA}$ (Te) < $2.257 \text{ \AA}$ (S) < $2.262 \text{ \AA}$ (Se)

Figure 5: Structure of $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{TePh}\}_2]^{2+}$ (Gysling and Luss, 1984).

< 2.276 Å (As) < 2.283 Å (Ge) < 2.316 Å (Si). The total mean Pt-X (trans to P) elongate in the sequence: 2.06 Å (X = O) < 2.12 Å (N) < 2.328 Å (S) < 2.360 Å (Si) < 2.422 Å (As) < 2.455 Å (Se) < 2.458 Å (Ge) < 2.627 Å (Te). The sum of all four (Pt-P(x2) + Pt-X(x2)) bond distances in these complexes with cis-configuration growing in the sequence: 8.55 Å (PtP₂O₂) < 8.72 Å (PtP₂N₂) < 9.17 Å (PtP₂S₂) < 9.35 Å (PtP₂Si₂) < 9.40 Å (PtP₂As₂) < 9.43 Å (PtP₂Se₂) < 9.48 Å (PtP₂Ge₂) < 9.75 Å (PtP₂Te₂). As can be seen inner coordination sphere in Pt(η²-P₂L)(η²-X₂L) complexes is more crowded when X = O, S or Si, and less crowded when X = Se, Ge or Te; than in the Pt(η²-P₂L)(XL)₂ complexes. Noticeable, in the both types of complexes the volume of the inner coordination sphere is equal (8.72 Å) when X = N.

There are at least two contributing factors to the size of the L–Pt–L chelate bond angles both ligands based. One is the steric constraints imposed by the ligand, and the other is the need to accommodate the imposed ring size. The effects of both steric and electronic factors can be seen from the values of the L–Pt–L chelate angles. These angles open in the sequences (mean values):

four-membered: 65.0° (SiOSi) < 66.0° (OCO) < 70.9° (PNP) < 73.5° (PCP) < 74.5° (SCS) < 77.8° (SeCSe) < 83.1° (GeGeGe) < 85.3° (SePSe);

five-membered: 78.9° (NC₂N, unsaturated) < 81.3° (OC₂O) < 81.8° (NC₂N, saturated) < 83.1° (SiC₂Si) < 83.8° (AsC₂As) < 84.0° (PCOP) < 86.1° (PC₂P) < 86.9° (PC₂Si) < 87.5° (SeSe₂Se) < 88.5° (PC₂Te) < 88.8° (SiSi₂Si) < 89.0° (SC₂S) < 89.7° (GeGe₂Ge);

six-membered: 85.8° (SCSCS) < 87.0° (SPNPS) < 89.7° (PC₃P) < 90.5° (OPOPO) < 91.2° (OBOBO) < 92.1° (SeC₃Se) < 93.5° (SC₃S) < 94.0° (PCNCP) < 95.2° (PCSiCP) < 95.7° (PCCNP) < 95.8° (PCSCP; POCNP) < 96.5° (PCCOP) < 97.0° (SPCPS);

seven-membered: 92.3° (SC₄S) < 95.8° (OC₄O) < 98.2° (PC₄P).

It is hoped that this review will serve to draw together common structural threads and stimulate activity in areas of particular interest.

Acknowledgements: This work was supported by the projects VEGA 1/0463/18, and APVV-15-0585.

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