Review Article **AJCR 2018 2:8**

American Journal of Chemical Research
(ISSN: 2573-0231)

Organodiphosphines in Monomeric PtP_2X_2 (X = OL, NL, CN, BL) Derivatives Structural Aspects

Milan Melník, Andrea Forgácsová, Peter Mikuš

Comenius University in Bratislava, Faculty of Pharmacy, Department of Pharmaceutical Analysis and Nuclear Pharmacy, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic
Comenius University in Bratislava, Faculty of Pharmacy, Toxicological and Antidoping Center, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic

ABSTRACT

In this review are classified and analyzed structural parameters of over seventy examples of monomeric PtP_2X_2 (X = OL, NL, CN or BL) derivatives in which P donor ligands are organodiphosphines. These complexes crystallize in four crystal systems: tetragonal (x1), triclinic (x11), orthorhombic (x19) and monoclinic (x40). The complexes were divided into the two groups: $Pt(\eta^2\text{-}P_2L)(XL)_2$ (X = O, N, CN or B) and $Pt(\eta^2\text{-}P_2L)(\eta^2\text{-}X_2L)$ (X = O or N). The chelating ligands create wide of metallocyclic rings and the effects of both steric and electronic factors influence on the values of L-Pt-L bite angles. The some cooperative effects were found and are discussed with trans-influence of the respective donor atoms.

Keywords: Structure, organodiphosphine, PtP2X2 (X = OL, NL, CN, BL), review

***Correspondence to Author:**
Milan Melník
Comenius University in Bratislava, Faculty of Pharmacy, Department of Pharmaceutical Analysis and Nuclear Pharmacy, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic
Comenius University in Bratislava, Faculty of Pharmacy, Toxicological and Antidoping Center, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic

How to cite this article:
Milan Melník, Andrea Forgácsová, Peter Mikuš. Organodiphosphines in Monomeric PtP_2X_2 (X = OL, NL, CN, BL) Derivatives Structural Aspects . American Journal of Chemical Research, 2018, 2:8

eSciPub LLC, Houston, TX USA.
Website: http://escipub.com/

Introduction

Due to the usefulness of platinum and its compounds considerable research activity has been invested in their synthesis and properties. This has included a considerable number of structural determinations which have helped to shed light on biological and other activity. Platinum exists in a wide range of oxidation states from zero to six, of which +2 and +4 are the most common, particularly in coordination chemistry. Structural parameters of over two thousand and five hundred platinum coordination complexes have been reviewed by us [1]. Recently we classified and analyzed structural parameters of stereoisomers of platinum coordination complexes [2]. Included are distortion (65%) cis-trans (30%), mixed isomers and ligand isomerism.

The aim of this review is to classify and analyze structural parameters of monomeric coordination complexes of platinum with an inner coordination spheres of PtP_2X_2 (X = OL, NL, CN, BL) in which P donor ligands are organodiphosphines. The primary source of information was Cambridge Crystallographic Database up to the end of october 2017.

Cis-PtP_2X_2 derivatives

There are over seventy examples of monomeric PtP_2X_2 (X = O, N, CN or B) complexes for which structural parameters are available and analyze in this paper.

There are almost forty derivatives with the PtP_2O_2 chromophore. On the basis of coordination mode of the respective donor ligands these derivatives can be divided into the two sub-groups: $Pt(\eta^2\text{-}P_2L)(OL)_2$ and $Pt(\eta^2\text{-}P_2L)(\eta^2\text{-}O_2L)$. These complexes crystallize in four crystal systems: tetragonal (x 1), triclinic (x 6), orthorhombic (x 12) and monoclinic (x 18).

There are thirteen examples with the cis-$Pt(\eta^2\text{-}P_2L)(OL)_2$ type. The structures are referred in the order of an increasing number of hetero-atoms in the P,P chelate rings. Such complexes are: $[Pt(\eta^2\text{-}Ph_2PCH_2PPh_2)(F_3CCOO)_2]$ [3], $[Pt(\eta^2\text{-}Ph_2PN(Me)PPh_2\}(ONO_2)_2]$ [4], $[Pt(\eta^2\text{-}(PhO)_2PN(Me)P(OPh)_2\}(OSO_2CF_3)_2]$ [5], $[Pt(\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(H_2O)_2](CF_3SO_3)_2$ [6], $[Pt(\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(OMe)_2]$ [7], $[Pt(\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(ONO_2)_2]$ [8], $[Pt(\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(OSO_2CF_3)_2]$(triclinic) [9] (monoclinic [10], $[Pt(\eta^2\text{-}Pr^i{}_2P(CH_2)_2PPr^i{}_2\}(acetate)_2]$ [11], $[Pt(\eta^2\text{-}Pr^i{}_2(CH_2)_2PPr^i{}_2\}(benzoate)_2]PhCOOH$ [11], $[Pt(\eta^2\text{-}1,2\text{-}(PhMeP)_2C_6H_4\}(OSO_2CF_3)_2]$ [12], $[Pt(\eta^2\text{-}Ph_2P(CH_2)_4PPh_2\}(H_2O)_2](CF_3SO_3)_2$ [13], and $[Pt(\eta^2\text{-}Ph_2P(C_{20}H_{12})PPh_2\}(OSO_2CF_3)_2].Et_2O$ [14]. Structure of $[Pt(\eta^2\text{-}Pr^i{}_2(CH_2)_2PPr^i{}_2\}(benzoate)_2]$ [11] is shown in Fig. 1 as an example. The chelating- P,P ligands plus two monodentate O donor ligands create cis-PtP_2O_2 chromophore. The chelating ligands form variety of metallocyclic rings with the mean values of P-Pt-P bite angles of 74.1º (PCP) [3], 70.0º (PNP) [4,5], 86.8º (PC_2P) [6-12] and 100.4º (PC_4P) [13,14]. The mean values of the remaining L-Pt-L bond angles are 85.8º (O-Pt-O), 95.5º and 175.0º (P-Pt-O). The mean values of Pt-L bond distances are 2.09 Å (O, trans to P) and 2.216 Å (P, trans to O).

There are twenty five examples with the cis-$Pt(\eta^2\text{-}P_2L)(\eta^2\text{-}O_2L)$ type. The structures are referred in the order of an increasing number of the heteroatoms in P,P-metallocyclic rings. Each Pt(II) atom has a square planar environment with varying degree of distortion build up by two homobidentate P,P and O,O donor ligands. The ligand arrays can be subdivided into the several groups. In $[Pt\{\eta^2\text{-}Ph_2PCH_2PPh_2\}\{\eta^2\text{-}oxalate\}].Me_2CO$ (Fig. 2) [15] the homobidentate P,P donor ligand creates four-membered and O,O donor ligand five-membered metallocyclic rings with the values of L-Pt-L bite angles of 74.0º (PCP) and 80.5º (OC_2O), respectively. The mean values of cis- and trans-P-Pt-O bond angles are 102.7 and 164.0º, respectively. The mean Pt-L bond distances are 2.06 Å (O, trans to P) and 2.215 Å (P, trans to O).

In another twelve complexes: $[Pt\{\eta^2\text{-}1,2\text{-}(PhMeP)_2C_6H_4\}\{\eta^2\text{-}HO(CH_2)_2OH\}]$. $(F_3CSO_3)_2$ [12], $[Pt\{\eta^2\text{-}1,2\text{-}(PhMeP)_2C_6H_4\}\{\eta^2\text{-}$

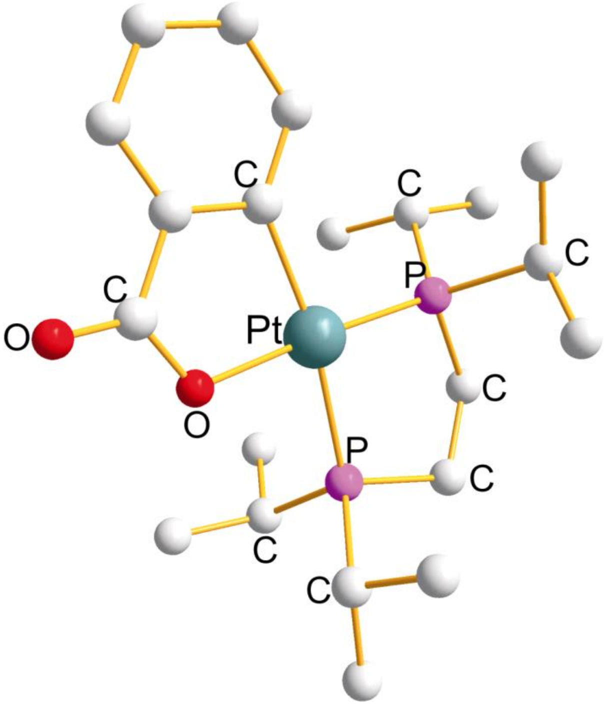

Figure 1. Structure of $[Pt(\eta^2\text{-}Pr^i{}_2(CH_2)_2PPr^i{}_2\}(benzoate)_2]$ [11]

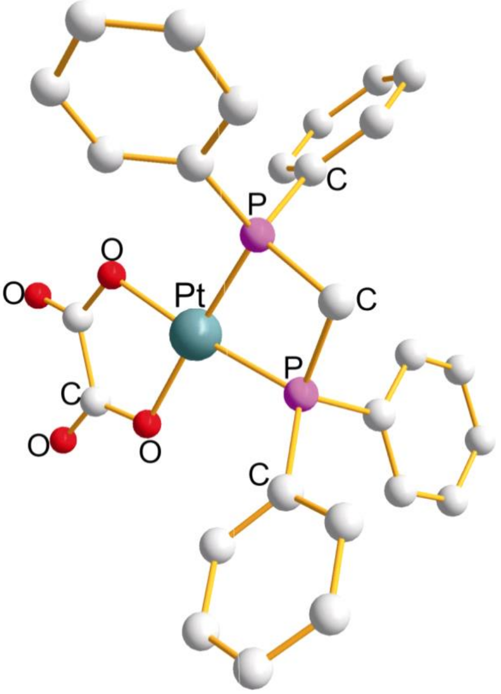

Figure 2. Structure of $[Pt\{\eta^2\text{-}Ph_2PCH_2PPh_2\}\{\eta^2\text{-}oxalate\}]$ [15]

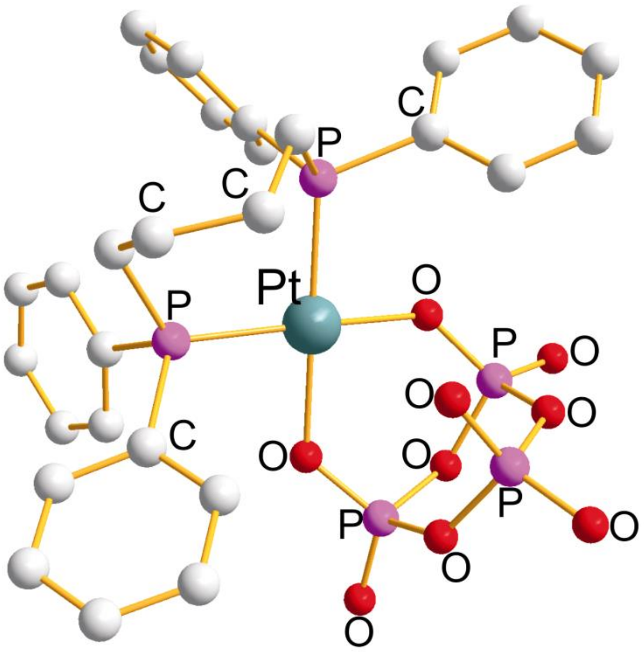

Figure 3. Structure of Pt{η^2-$Ph_2P(CH_2)_4PPh_2$}{η^2-O_9P_3}]$^-$ [21]

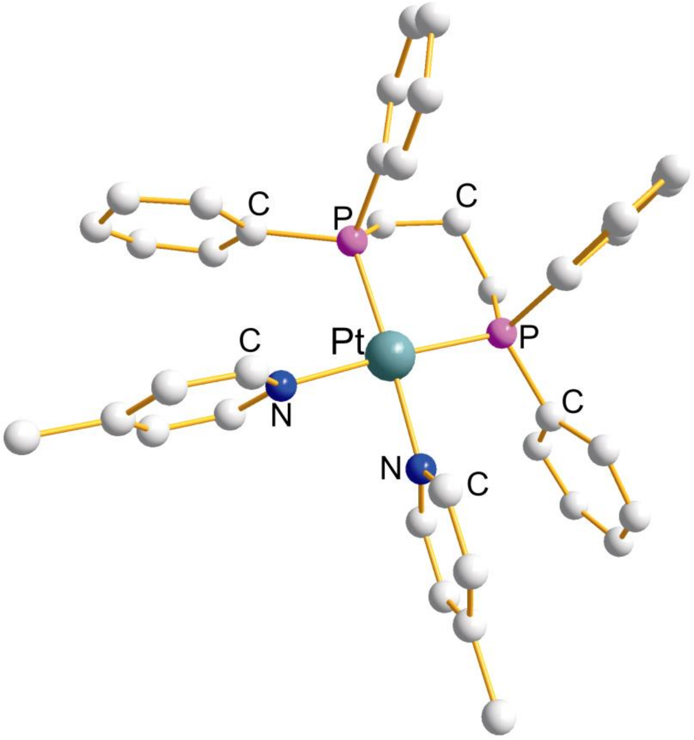

Figure 4. Structure of [Pt{η^2-$Ph_2P(CH_2)_3PPh_2$}(NC_6H_7)$_2$]$^{2+}$ [39]

OCH$_2$CH(O)CH$_2$OH}].2MeOH [16], [Pt{η^2-cy$_2$P(CH$_2$)$_2$Pcy$_2$}{η^2-oxalate}].MeCN [17], [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-C$_{14}$H$_{20}$O$_2$}].CHCl$_3$ [18], [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-C$_{20}$H$_{14}$O$_2$}] [19], [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-C$_{12}$H$_{10}$B$_2$O$_3$)}] [20], [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-C$_{14}$H$_{14}$B$_2$O$_5$}] [20], (PPh$_4$)[Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-O$_9$P$_3$}]MeCN.CH$_2$Cl$_2$ [21], [Pt{η^2-Ph$_2$(CH$_2$)$_2$PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}] [22], [Pt{η^2-Ph$_2$PCH(Me)$_2$CHPPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}] [22], [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-C$_{32}$H$_{20}$O$_2$}].CH$_2$Cl$_2$ [23], and [Pt{η^2-Ph$_2$P(CH$_2$)$_2$PPh$_2$}{η^2-squ}].MeCN [24], the homobidentate P,P-donor ligands create five-membered metallocyclic rings (PC$_2$P) [12,16-24] and together with five-(OC$_2$O) [12,16-19], six-(OBOBO) [20], (OPOPO) [21], and seven-(OC$_4$O) [22-24] membered rings build up a distorted square planar environment about each Pt(II) atom. The mean values of the respective metallocyclic rings are: 87.3º (PC$_2$P) [12,16-24], 81.5º (OC$_2$O) [12,16-19], 91.2º (OBOBO) [20], 89.8º (OPOPO) [21] and 90.3º (OC$_4$O) [22-24].

In another six examples: [Pt{η^2-Ph$_2$P(CH$_2$)$_3$PPh$_2$}{η^2-O$_2$CO}] [25], [Pt{η^2-Ph$_2$P(CH$_2$)$_3$PPh$_2$}{η^2-O$_2$CO}].CH$_2$Cl$_2$ [25], [Pt{η^2-cy$_2$P(CH$_2$)$_3$Pcy$_2$}{η^2-O$_2$CO}]toluene [26], [Pt{η^2-Ph$_2$P(CH$_2$)$_3$PPh$_2$}{η^2-oxalate}] [27], [Pt{η^2-Ph$_2$P(CH$_2$)$_3$PPh$_2$}{η^2-malonate}] [28], and [Pt{η^2-Ph$_2$P(CH$_2$)$_3$PPh$_2$}{η^2-C$_{44}$H$_{54}$O$_4$}].CH$_2$Cl$_2$ [29], homobidentate P,P donor ligands creates six-membered metallocyclic rings (PC$_3$P) and together with homobidentate O,O donor ligands with four-(OCO) [25,26], five-(OC$_2$O) [27], six-(OC$_3$OI) [28] and even eight-(OC$_5$O) [29] membered metallocyclic rings completed cis-PtP$_2$O$_2$ chromophores. The mean values of the respective metallocycles are: 95.8º (PC$_3$P) [25-29], 66.0º (OCO) [25,26], 82.0º (OC$_2$O) [27], 90.1º (OC$_3$O) [28], and 95.3º (OC$_5$O) [29].

In remaining six complexes: [PPh$_3$N][Pt{η^2-Ph$_2$P(CH$_2$)$_4$PPh$_2$}{η^2-O$_9$P$_3$}]MeCN.0.5CH$_2$Cl$_2$ [21], [Pt{η^2-Ph$_2$P(C$_{12}$H$_8$)PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}].CH$_2$Cl$_2$ [30], [Pt{η^2-Ph$_2$P(C$_{12}$H$_{22}$)PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}].toluene [31], [Pt{η^2-Ph$_2$P(C$_{20}$H$_{18}$)PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}].toluene [32], [Pt{η^2-Ph$_2$P(C$_8$H$_{12}$)PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}].CH$_2$Cl$_2$ [32], and [Pt{η^2-Ph$_2$P(C$_{28}$H$_{20}$)PPh$_2$}{η^2-C$_{20}$H$_{12}$O$_2$}].CHCl$_3$ [32], homobidentate P,P donor ligands creates seven-(PC$_4$P) membered rings and together with six-(OPOPO) [21] and seven-(OC$_4$O) [30-32] membered metallocyclic rings completed cis-PtP$_2$O$_2$ chromophore. Structure of Pt{η^2-Ph$_2$P(CH$_2$)$_4$PPh$_2$}{η^2-O$_9$P$_3$}]$^{-}$ [21] is shown in Fig. 3 as an example. The mean values of the respective metallocycles are: 100.5º (PC$_4$P) [21,30-32], 91.3º (OPOPO) [21], amd 89.8º (OC$_4$O) [30-32].

There are cooperative effects between cis-P-Pt-P (metallocycle) and cis-P-Pt-O bond angles, the former uncloses with the growing size of the metallocycle and the latter closes as expected. The mean values of cis-P-Pt-P and cis-P-Pt-O are: 74.0º (PCP) and 102.7º (P-Pt-O); 86.8º (PC$_2$P) and 94.8º (P-Pt-O); 95.8º (PC$_3$P) and 91.5º(P-Pt-O); 100.4º (PC$_4$P) and 84.5º (P-Pt-O). The trans-P-Pt-O bond angles range from 164.0º to 178.0º. The mean values of Pt-L bond distances are 2.06 Å (O, trans to P) and 2.215 Å (P, trans to O).

There are twenty five examples with the PtP$_2$N$_2$ chromophore. These complexes on the basis of the coordination mode of the respective donor ligands can be divided into the two groups: Pt(η^2-P$_2$L)(NL)$_2$ and Pt(η^2-P$_2$L)(η^2-N$_2$L). These complexes crystallize in three crystal systems: triclinic (x 3), orthorhombic (x 7) and monoclinic (x 15).

There are eighteen complexes of the cis-Pt(η^2-P$_2$L)(NL)$_2$ type. The structures are referred in the order of an increasing numbers of heteroatoms in the P,P-metallocycles. Monoclinic Pt{η^2-(PhO)$_2$PNP(OPh)$_2$}(NC$_8$H$_{11}$)$_2$](F$_3$CSO$_3$)$_2$ [5] is only example in which homobidentate P,P donor ligand creates four-membered metallocyclic ring with the value of P-Pt-P bite angle of 70.5º (PNP) and pair of monodentate N donor ligands completed a distorted square planar environment, cis-PtP$_2$N$_2$.

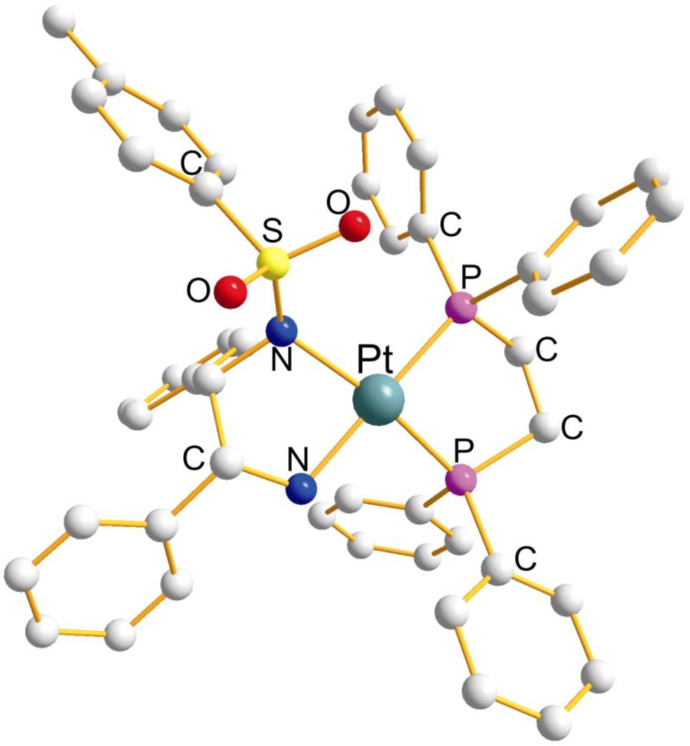

Figure 5. Structure of [Pt{η^2-$Ph_2P(CH_2)_2PPh_2$}(η^2-$N_2C_{21}H_{20}O_2S$)] [45]

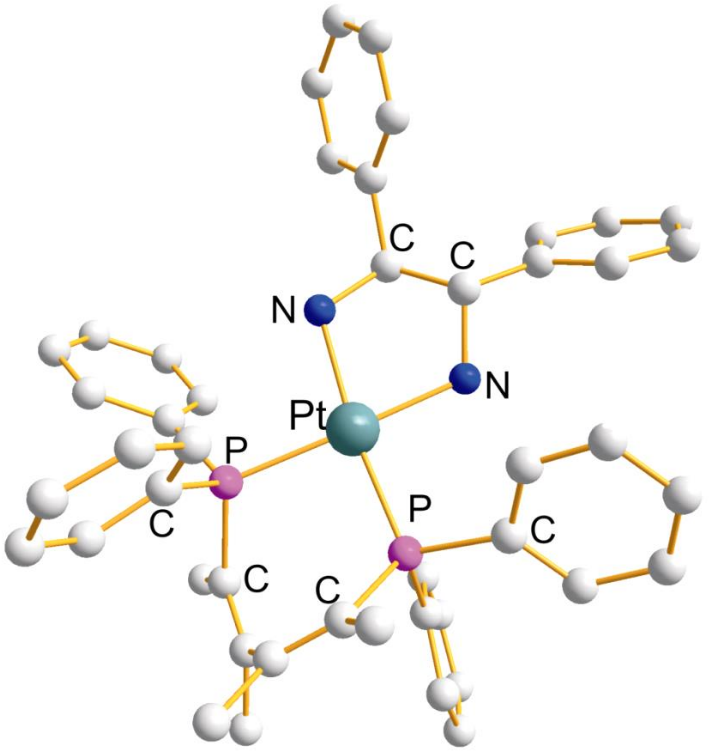

Figure 6. Structure of [Pt{η^2-$Ph_2P(C_8H_{12})PPh_2$}{η^2-$N_2C_{14}H_{16}$}]$^{2+}$ [47]

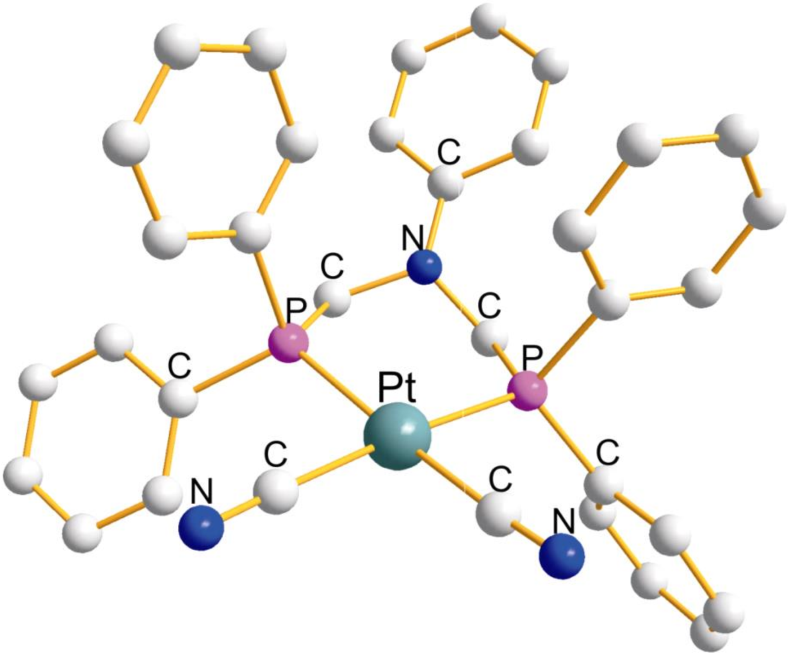

Figure 7. Structure of [Pt{η^2-$Ph_2PCH_2N(Ph)CH_2PPh_2$}$(CN)_2$] [51]

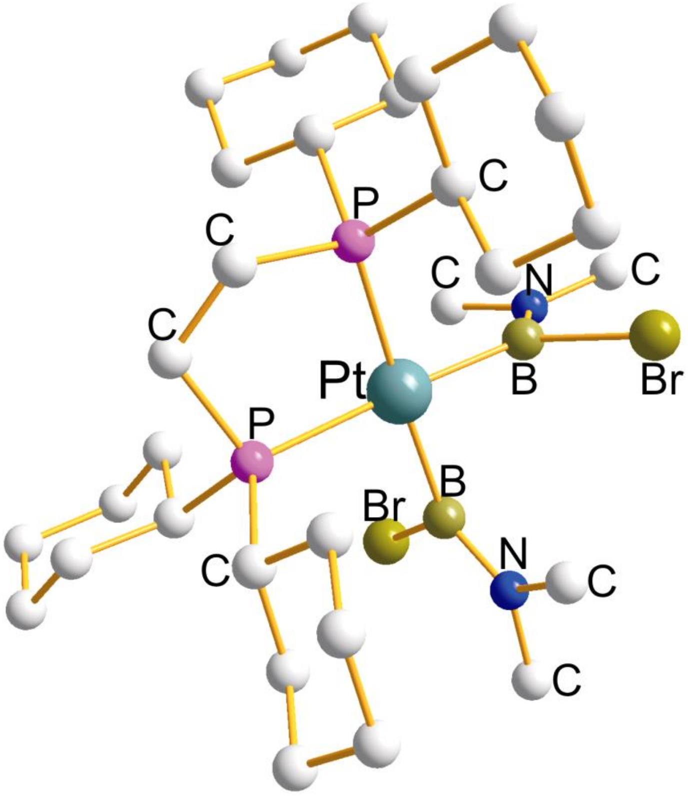

Figure 8. Structure of [Pt{η^2-$cy_2P(CH_2)_2Pcy_2$}{$B(NMe_2)Br$}$_2$] [52]

In four examples: $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(3,5\text{-}Me_2pz)_2]$ [33], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(3,5\text{-}Me_2pzH)_2](BF_4)_2.CH_2Cl_2$ [34], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(p\text{-}O_2NC_6H_4SNSN)_2]$ [35] and $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(pz)_2](BF_4)_2.CHCl_3.H_2O$ [36] homobidentate P,P donor ligands creates five-membered metallocyclic rings with the mean P-Pt-P bite angles of 85.8º (PC_2P). Two monodentate N donor ligands completed a distorted square planar environment about each Pt(II) atom (cis-PtP_2N_2). The mean values of remaining L-Pt-L bond angles are 90.5º (N-Pt-N), 91.8 and 176.2º (P-Pt-N). The mean Pt-L bond distances are 2.08 Å (N, trans to P) and 2.244 Å (P, trans to N).

In another eleven examples: $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(quinoline)_2](F_3CSO_3)_2$ [37], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(pz)_2](F_3CSO_3)_2$ [38], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(pyridine)_2](F_3CSO_3)_2.CH_2Cl_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_6H_7)_2](CF_3SO_3)_2.CH_2Cl_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_6H_7O)_2](CF_3SO_3)_2.H_2O$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_9H_{14})_2](CF_3SO_3)_2.CH_2Cl_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_6H_{10})_2](CF_3SO_3)_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_{10}H_9)_2](CF_3SO_3)_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_6H_7O)_2](CF_3SO_3)_2$ [39], $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(N_2C_7H_8O)_2](CF_3SO_3)_2$ [39] and $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_3\}(N_2C_5H_6)_2](CF_3SO_3)_2.H_2O$ [40] the chelating P,P donor ligands creates six-membered metallocycles with the mean P-Pt-P bite angles of 93.3º (PC_3P). The pairs of monodentate N- donor ligands completed cis-PtP_2N_2 chromophore. Structure of $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_3PPh_2\}(NC_6H_7)_2]^{2+}$ [39] is shown in Fig. 4 as an example. The mean values of the remaining L-Pt-L bond angles are 86.2º (N-Pt-N), 90.2º and 176.0º (P-Pt-N). The mean values of Pt-L bond distances are 2.12 Å (N, trans to P) and 2.267 Å (P, trans to N).

Triclinic $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_4PPh_2\}(NO_2)_2]$ [41] is only example in which chelating P,P- donor ligand creates seven-membered metallocycle with the value of P-Pt-P bite angle of 94.9(2)º (PC_4P). Two NO_2^- groups completed a distorted square planar environment about the Pt(II) atom (cis-PtP_2N_2). The value of N-Pt-N bond angle is 84.6(7)º. The mean values of Pt-L bond distances are 2.11 Å (N, trans to P) and 2.268 Å (P, trans to N).

There are eight examples of the cis-$Pt(\eta^2\text{-}P_2L)(\eta^2\text{-}N_2L)$ type. The ligand arrays can be subdivided into the three groups: monoclinic $[Pt\{\eta^2\text{-}Ph_2PCH_2PPh_2\{(\eta^2\text{-}N_2C_{12}H_8)](PF_6)_2$ [42] is only example in which chelating P,P donor ligand creates four-membered metallocycle with the value of P-Pt-P bite angle of 74º (PCP). The chelating N,N donor ligand creates five-membered metallocycle with the value of N-Pt-N bite angle of 82º (NC_2N) and completed a distorted square planar environment about the Pt(II) atom (cis- PtP_2N_2).

In another four complexes: $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}sulfonamide)].CH_2Cl_2$ [43], $[Pt\{\eta^2\text{-}Ph_2PCH(Me)CH(Me)PPh_2\}(\eta^2\text{-}N_2C_{10}H_8)](PF_6)_2.1.8CH_2Cl_2$ [44], $[Pt\{\eta^2\text{-}Ph_2PCH(Me)CH(Me)PPh_2\}(\eta^2\text{-}N_2C_{12}H_8)](BF_4)_2.CH_2Cl_2$ [44] and $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}N_2C_{21}H_{20}O_2S)].CH_2Cl_2$ [45] both chelating P,P and N,N donor ligands creates five-membered metallocycles with the mean values of L-Pt-L bite angles of 84.6º (PC_2P) and 78.9º (NC_2N). Structure of $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}N_2C_{21}H_{20}O_2S)]$ [45] is shown in Fig. 5 as an example. The mean values of remaining L-Pt-L bond angles are 98.3º and 175.7º (P-Pt-N). The mean values of Pt-L bond distances are 2.11 Å (N, trans to P) and 2.254 Å (P, trans to N).

In the remaining three examples: $[Pt\{\eta^2\text{-}Ph_2P(C_{12}H_8)PPh_2\}\{\eta^2\text{-}N_2C_{14}H_{16}\}]Cl_2CH_2Cl_2.H_2O$ [46], $[Pt\{\eta^2\text{-}Ph_2P(C_8H_{12})PPh_2\}\{\eta^2\text{-}N_2C_{14}H_{16}\}](ClO_4)_2.CH_2Cl_2$ [47] and $[Pt\{\eta^2\text{-}Ph_2P(C_{28}H_{20})PPh_2\}\{\eta^2\text{-}NC_{14}H_{16}\}](F_3CSO_3)_2.CHCl_3.MeOH$ [48] each chelating P,P donor ligand creates seven-membered metallocycle with the mean P-Pt-P bite angle of 92.5º (PC_4P) and each chelating N,N-donor ligand creates five-membered metallocycle with the mean N-Pt-N bite angle of

81.5º (NC_2N). Structure of $[Pt\{\eta^2\text{-}Ph_2P(C_8H_{12})PPh_2\}\{\eta^2\text{-}N_2C_{14}H_{16}\}]^{2+}$ [47] is shown in Fig. 6 as an example. The values of remaining L-Pt-L bond angles are 93.5º and 175.5º (P-Pt-N). The values of Pt-L bond distances are 2.10 Å (N, trans to P) and 2.268 Å (P, trans to N).

There are four monoclinic examples with the cis-$Pt(\eta^2\text{-}P_2L)(CN)_2$ type. The chelating P,P ligand arrays can be subdivided into the three groups. In $[Pt\{\eta^2\text{-}Ph_2PCH_2PPh_2\}(CN)_2]$ [49] the chelating P,P donor ligand creates four-membered metllocycle with the P-Pt-P bite angle of 70.7º (PCP). In $[Pt\{\eta^2\text{-}Ph_2P(C_6H_4)PPh_2\}(CN)_2]$ [50] the chelating ligand creates five-membered metallocycle with the value of P-Pt-P bite angle of 86.4º (PC_2P). In $[Pt\{\eta^2\text{-}Ph_2PCH_2N(Ph)CH_2PPh_2\}(CN)_2]$ (Fig. 7) [51] the chelating ligand creates six-membered metallocycle 90.2º (PCNCP). The mean values of L-Pt-L bond angles are 93.8º (C-Pt-C) and 88.4º (P-Pt-C). The mean values of Pt-L bond distances are 2.00 Å (C, trans to P) and 2.335 Å (P, trans to C).

There are five examples with the $Pt(\eta^2\text{-}P_2L)(BL)_2$ type. The chelating P,P donor ligand arrays can be subdivided into the three groups. In monoclinic $[Pt\{cy_2PCH_2Pcy_2\}\{B(NMe_2)Br\}_2]$ [52] the chelating P,P donor ligand creates four-membered metallocycle with the P-Pt-P bite angle of 73.8º (PCP) and pair of monodentate B donor ligands build up a distorted square planar environment about the Pt(II) atom (cis-PtP_2B_2). In another monoclinic $[Pt\{\eta^2\text{-}cy_2P(CH_2)_2Pcy_2\}\{B(NMe_2)Br\}_2]$toluene [52] and triclinic $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}\{B(1,2\text{-}O_2C_6H_4)\}_2]$ [53] each chelating P,P donor ligand creates five-membered metallocycle with the P-Pt-P bite angle of 85.4º (PC_2P). In remaining two complexes, monoclinic $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_4PPh_2\}\{B(1,2\text{-}O_2C_6H_4)\}_2]$ [53] and triclinic $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_4PPh_2\}(BF_2)_2]$ [41] the chelating ligand creates seven-membered metallocycle with the mean P-Pt-P bond angles of 98.2º (PC_4P). Structure of $[Pt\{\eta^2\text{-}cy_2P(CH_2)_2Pcy_2\}\{B(NMe_2)Br\}_2]$ [52] is shown in Fig. 8 as an example. The mean values of L-Pt-L bond angles are 79.7º (B-Pt-B), 94.0º and 169.4º (P-Pt-B). The mean values of Pt-L bond distances are 2.045 Å (B, trans to P) and 2.332 Å (P, trans to P).

Conclusions

There are over seventy examples of monomeric Pt(II) complexes with cis-PtP_2X_2 inner coordination. The P donor ligands are organodiphosphines and X donor ligands are OL (37 examples), NL (25 examples), CN (4 examples) or BL (5 examples). These complexes crystallize in four crystal systems: tetragonal (x 1), triclinic (x 11), orthorhombic (x 19) and monoclinic (x 40). On the bases of coordination mode of the respective donor ligands these complexes can be divided into the two sub-groups: $Pt(\eta^2\text{-}P_2L)(XL)_2$ (X = O, N, CN or B) and $Pt(\eta^2L)(\eta^2\text{-}X_2L)$ (X = O or N).

The total mean Pt-P (trans to X) bond distances elongate in the order: 2.215 Å (X = O) < 2.260 Å (N) < 2.332 Å (B) < 2.335 Å (C). The total mean Pt-X (trans to P) elongate in the order: 2.01 Å (X = C) < 2.04 Å (B) < 2.075 Å (O) < 2.09 Å (N). The sum of all four (Pt-P(x2)+Pt-X(x2)) bond distances growing quite well with covalent radii of X atoms in the order: 8.58 Å (X = O, 0.73 Å) < 8.70 Å (N, 0.75 Å) C, 0.77 Å) < 8.75 Å (B, 0.82 Å).

The chelating P,P; O,O and N,N donor ligands create variations of the metallocycles and the effects of both steric and electronic factors can be seen from the mean values of the L-Pt-L bite angles, which open in the orders:

P-Pt-P: 70.0º (PNP) < 74.0º (PCP) < 86.8º (PC_2P) < 95.8º (PC_3P) < 100.4º (PC_4P);

O-Pt-O: 66.0º (OCO) < 81.3º (OC_2O) < 90.0º (OC_3O. OC_4O) < 90.5º (OPOPO) < 91.2º (OBOBO) < 95.8º (OC_3O);N-Pt-N: 78.9º (NC_2N, unsaturated) < 81.5º (NC_2N, saturated).

In the series of $Pt(\eta^2\text{-}P_2L)(\eta^2\text{-}O_2L)$ complexes is cooperative effect between cis-P-Pt-P (metallocycle) and cis-P-Pt-O bond angles (mean values). The former unclose and the latter close: 74.0º (PCP) and 102.7º; 86.8º (PC_2P) and 94.8º; 95.8º (PC_3P) and 91.5º; 100.4º (PC_4P) and 84.5º.

In the series of $Pt(\eta^2-P-L)(XL)_2$ complexes is cooperative effect between cis-X-Pt-X and P-Pt-X bond angles (mean values). The former unclose and the latter close: 79.7º and 94.0º (X = B); 85.8º and 93.5º (X = O); 87.1º and 93.0º (X = N); 93.8º and 88.4º (X = C).

During the collection and organization of the data it has become evident that in spite of the increasing availability of data retrieval systems, the trucking of relevant structural data is not always simple. Poorly chosen key words for indexes appear to be no problem which results in effective invisibility of some material from a structural point of view. Some original papers are lacking important information such as atomic coordinates and analysis of intermolecular distances. Increasingly such data are also being relegated to supplementary material. In view of these limitations we believe that a review such as this can continue to serve a useful function by centralizing available material and delineating areas worthy of further investigation. Related review of cis-PtP_2Cl_2 derivatives in which P-donor ligands are organodiphosphines is in progress.

Acknowledgements

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

Abbrevations

$C_{12}H_{10}B_2O_3$	1,3-diphenyl-1,3-dibora-2-oxapropane-1,3-diolate
	1,3-bis(4-acetylphenyl)-1,3-dibora-2-oxapropano-1,3-diolate
$C_{14}H_{20}O_2$	3,5-di-terc-butylbenzene-1,2-diolate
	2,2´-binaphthyl-1,1´-diolate
$C_{20}H_{14}O_6$	3,4-bos(benzyloxy)-5-(1,2-dioxyethyl)furan-2(5H)-one
	3,3´-diphenyl-2,2´-binaphthyl-1,1´-diolate
	5,11,17,23-tetra-teriôbutyl-27,28-dihydroxypentacyclo [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-l(25),3,5,7(28);9,11,13(27), 15,17,19(26),21,23-dpdecaeme25,26-diolate
	3,5-dimethylpyrazol-2-yl
$N_2C_{10}H_8$	2,2´-bipyridine
$N_2C_{12}H_8$	1,10-phenanthroline
$N_2C_{14}H_{16}$	1,2-diphenylethane-1,2-diamine
$N_2C_{21}H_{20}O_2S$	2-amido-1,2-diphenylethyl-1-p-toluene-sulfonamidate
$N_2C_5H_6$	2-aminopyridine
$N_2C_7H_{10}$	N,N-dimethylpyridin-4-amine
$N_2C_7H_8O$	(pyridine-4-yl)acetamide
$NC_{10}H_9$	4-phenylpyridine
NC_6H_7	4-methylpyridine
NC_7H_7O	4-acetylpyridine
NC_6H_7O	4-methoxypyridine
NC_8H_{11}	2,6-dimethylaniline
NC_9H_{14}	4-terc-butylpyridine
O_9P_3	cyclotriphosphate
$Ph_2P(C_{12}H_8)PPh_2$	2,2´-bis(diphenylphosphino)1,1´-biphenyl
$Ph_2P(C_{12}H_8)PPh_2$	2,2´-bis(diphenylphosphino)-1,1´-biphenyl
$Ph_2P(C_{20}H_{12})PPh_2$	1,1´-binaphtalene-2,2´-diylbis(diphenylphosphine)
$Ph_2P(C_{20}H_{18})PPh_2$	1,2-bis(diphenylphosphino)phenylmethylene) cyclohexane
$Ph_2P(C_{28}H_{20})PPh_2$	1,4-bis(diphenylphosphino)1,2,3,4-tetraphenyl-1,3-butadiene
$Ph_2P(C_6H_4)PPh_2$	1,2-bis(diphenylphosphino)benzene
$Ph_2P(C_8H_{12})PPh_2$	1,2-bis(diphenylphosphino)1,2,3,4-tetramethyl-1,3-butadiene
$Ph_2P(C_8H_{12})PPh_2$	2,5-bis(diphenylphosphino)-3,4-dimethylhexa-2,4-diene
$Ph_2PC_{12}H_{22})PPh_2$	1,2-bis((1-diphenylphosphino)prop-1-ylidene) cyclohexane
$Ph_2PCH_2N(Ph)CH_2PPh_2$	N,N-bis((diphenylphosphino)methyl)niline
$Ph_2PN(Me)PPh_2$	bis(diphenylphosphino)methylamine
$(PhO)_2PN(Me)P(OPh)_2$	1,1,3,3-tetrakis(phenox&)-2-metyldiphosphazane
pz	pyrazol-2-yl
squ	silasesquinoxanate

v texte do horneho indexu

1. Konno M., Ohfuchi R., Shirotani I., Yamochi Y., Saito Z., Z. Kristallogr., 1997, 212, 121-125.
2. Aoki K., Hu N.H., Tokuno T., Adeyemo A.O., Williams O.N., Inorg. Chim. Acta, 1999, 290, 145-152.

3. Gysling H.J., Luss H.R., Organometallics, 1984, 3, 596-598.
4. Bugarcic Z., Norén B., Oskarsson Å., Stälhanske C., Elding L.I., Acta Chem. Scand., 1991, 45, 361-366.

REFERENCES

1. Holloway, C.E.; Melník, M. Structural aspect of platinum coordination compounds:part V. Dimeric and Oligomeric platinum derivatives. Rev Inorg Chem. **2005**, *25*, 93-270.
2. Melník, M. ; Holloway, C.E. Stereochemistry of platinum coordination compounds. Coord Chem Rev. **2006**, *250*, 2261-2270.
3. Tan, A.L.; Low, P.M.N.; Zhou, Z.Y.; Zheng, W.; Wu, B.M.; Mak, T.E.W.; Hor, T.S. Bis(carboxylato) complexes of platinum(II). Structural and bonding analysis of $[Pt(O_2CR)_2(L–L)][L–L = 2PPh_3, Ph_2PCH_2PPh_2$ or $Fe(C_5H_4PPh_2)_2$; R = Me, CF_3, Pr^i or Ph]. J Chem Soc, Dalton Trans. **1996**, 2207-2214.
4. Anandhi, Z.; Holbert, T.; Lueng, D.; Sharp, P.R. Platinum and Palladium Imido and Oxo Complexes with Small Natural Bite Angle Diphosphine Ligands. Inorg Chem. **2003**, *42*, 1282-1295.
5. Xia, A.; Sharp, P.R. Diphosphazane supported platinum(II) triflate, amine, and amido complexes: synthesis and X-ray crystal structures. Polyhedron. **2002**, *21*, 1305-1310.
6. Fallis, S.; Anderson, G.A.; Rath, N.P. Nucleophilic attack on or displacement of coordinated 1,5-cyclooctadiene. Structures of platinum complexes $[Pt\{.sigma.:.eta.2\text{-}C_8H_{12}(PPh_3)\}(dppe)][ClO_4]_2$ and $[Pt(dppe)(H_2O)_2][O_3SCF_3]_2$. Organometallics. **1991**, *10*, 3180-3184.
7. Bryndza, H.E.; Calabrese, J.C.; Marsi, M.; Roc, D.C.; Tam, W.; Bercaw, J.E. .beta.-Hydride elimination from methoxo vs. ethyl ligands: thermolysis of $(dppe)Pt(OCH_3)_2$, $(dppe)Pt(CH_2CH_3)(OCH_3)$ and $(dppe)Pt(CH_2CH_3)_2$. J Am Chem Soc. **1986**, *108*, 4805-4813.
8. Arendse, M.J.; Anderson, G.K.; Rath, N.R. [Ethylene-1,2-bis(diphenylphosphine)-P,P′]dinitratoplatinum(II) and cis-bis[(diphenylphosphinomethyl)diphenylphosphine oxide-O,P]platinum(II) dinitrate dehydrate. Acta Cryst Sect C, Cryst Struct Commun. **2001**, *57*, 237-239.
9. Brunkan, N.M.; White, P.S.; Gagne, M.R. Thermodynamic and Kinetic Relationships between Lewis Acid−Lewis Base Complexes Relevant to the $P_2Pt(OTf)_2$-Catalyzed Diels−Alder Reaction. Organometallics. **2002**, *21*, 1565-1575.
10. Pantcheva, I.; Osakada, K. Synthesis and Reactivity of a Platinum(II) Complex with a Chelating Dehydro(arylboronic anhydride) Ligand. Transmetalation of Arylboronic Acid. Organometallics. **2006**, *25*, 1735-1741.
11. Manbeck, K.A.; Kundu, S.; Walsh, A.P.; Brennessel, W.W.; Jones, W.D. Carbon–Oxygen Bond Activation in Esters by Platinum(0): Cleavage of the Less Reactive Bond. Organometallics. **2012**, *31*, 5018-5024.
12. Appellt, A.; Arcaratman, V.; Willis, A.C.; Wild, S.B. Alcohol complexes of platinum(II). Syntheses and crystal structures of [S-(R*,R*)]-(+)589-$[Pt(OSO_2CF_3)_2[1,2\text{-}C_6H_4(PMePh)_2]$ and [S-(R*,R*)]-(+)589-$[Pt(HOCH_2CH_2OH)$ $[1,2\text{-}C_6H_4(PMePh)_2](CF_3SO_3)_2$. Tetrahedron Assym. **1990**, *1*, 9-12.
13. Song, L.Ch.; Jin, G.X.; Wang, H.T.; Zhang, W.X.; Hu, Q.M. Self-Assembly of Cationic Pd(II)/Pt(II) Metallomacrocycles Containing Tetrahedral C_2Co_2Clusters from Rigid Cluster-Bridged Bipyridine $(4\text{-}C_5H_4N)_2C_2Co_2(CO)_6$ and Diphosphine- or Diarsine-Chelated Pd(II)/Pt(II) Complexes $[M(dppb)(H_2O)_2][OTf]_2$ (M = Pd, Pt), $[Pd(dpab)(H_2O)(OTf)][OTf]$, and $[Pt(dpab)(H_2O)_2][OTf]_2$. Organometallics. **2005**, *24*, 6464-6471.
14. Mc Bee, J.L.; Bell, A.T.; Tilley, T.D. Mechanistic Studies of the Hydroamination of Norbornene with Electrophilic Platinum Complexes: The Role of Proton Transfer. J Am Chem Soc. **2008**, *130*, 16562-16571.
15. Arendse, M.J.; Anderson, G.K.; Rath, N.P. Oxidative degradation of the ascorbate anion in the presence of platinum and palladium. Formation and structures of platinum and palladium oxalate complexes. Polyhedron. **2001**, *20*, 2495-2503.
16. Appelt, A.; Willis, A.C.; Wild, S.B. Glycerolato-1O,2O complexes of platinum(II): solid and solution state structures of [(R*,R*),(R*)]-(±)[PtOCH2CH(O))CH2OH{1,2-C6H4(PMePh)2}]·MeOH. J Chem Soc, Chem Commun. **1988**, 938-940.
17. Mague, J.T.; Recatto, C.A.; Fink, M.J. Solid state structure of oxalato-(bis(dicyclohexylphosphino)-ethane) platinum(II)-acetonitrile solvate. J Chem Crystallogr. **1994**, *24*, 193-195.
18. Best, J.; Sazanovich, I.V.; Adams, H.; Bennett, R.D.; Davies, E.S.; Meijer, A.J.H.M.; Towrie, M.; Tikhomirov, S.A.; Bouganov, O.V.; Ward, M.D.; Weinstein, J.A. Structure and Ultrafast Dynamics of the Charge-Transfer Excited State and Redox Activity of the Ground State of Mono- and

Binuclear Platinum(II) Diimine Catecholate and Bis-catecholate Complexes: A Transient Absorption, TRIR, DFT, and Electrochemical Study. Inorg Chem. **2010**, *49*, 10041-10056.

19. Bergamini, P.; Marchesi, E.; Bertolasi, V.; Fogagnolo, M.; Scarpantonio, L.; Manfredini, S.; Vertuani, S.; Canella, A. New Coordination Modes of L-Ascorbic Acid and Dehydro-L-ascorbic Acid as Dianionic Chelating Ligand for Platinum. Eur J Inorg Chem. **2008**, 529-537.
20. Pantcheva, I.; Osakada, K. Synthesis and Reactivity of a Platinum(II) Complex with a Chelating Dehydro(arylboronic anhydride) Ligand. Transmetalation of Arylboronic Acid. Organometallics. **2006**, *25*, 1735-1741.
21. Kamimura, S.; Kuwata, S.; Iawasaki, M.; Ishii, Y. Syntheses, structures and solution behaviour of cyclotriphosphato complexes of Pd(II), Pt(II) and Pt(IV). Dalton Trans. **2003**, 2666-2673.
22. Brunkan, J.M.; White, P.S.; Gagne, M.R. Platinum(II) Complexes with Constructive and Destructive Interaction of Diphosphane and Binaphthol Ligands. Angew Chem, Int Ed Engl. **1998**, *37*, 1579-1582.
23. Becker, J.J.; White, P.S.; Gagne, M.R. Synthesis and Characterization of Chiral Diphosphine Platinum(II) VANOL and VAPOL Complexes. Organometallics. **2003**, *22*, 3245-3249.
24. Abbenhuis, H.C.L.; Burrows, A.D.; Kooijman, H.; Lutz, M.; Palmer, M.T.; van Santen, R.A.; Spek, A.L. Synthesis and structural characterisation of platinum silasesquioxane complexes. J Chem Soc, Chem Commun. **1998**, 2627-2628.
25. Andrews, M.A.; Gould, G.O.; Klooster, W.T.; Koenig, K.S.; Woss, E.J. Syntheses, Spectra, and Structures of (Diphosphine)platinum(II) Carbonate Complexes. Inorg Chem. **1996**, *35*, 5478-5483.
26. Nicolas, E.; Nocton, G.; Mezailles, N. CO Activation by (Diphosphane)platinum(0): Carbonate and Acetone Formation – Experimental and Mechanistic Study. Eur J Inorg Chem. **2013**, 4000-4007.
27. Praingam, N.; Anderson, G.K.; Rath, N.P. Base-promoted synthesis of monometallic and bimetallic platinum complexes containing chelating O,O- or S,S-donor ligands. Inorg Chim Acta. **2007**, *360*, 1767-1770.
28. Andrews, M.A.; Voss, E.J.; Gould, G.L.; Klooster, W.T.; Koetzle, T.F. Regioselective Complexation of Unprotected Carbohydrates by Platinum(II): Synthesis, Structure, Complexation Equilibria, and Hydrogen-Bonding in Carbonate-Derived Bis(phosphine)platinum(II) Diolate and Alditolate Complexes. J Am Chem Soc. **1994**, *116*, 5730-5740.
29. Kotzen, N.; Goldberg, I.; Lipstman, S.; Vigalok, A. Unexpected Pt^{II} Migration between the Calixarene Oxygen Atoms. Inorg Chem. **2006**, *45*, 5266-5268.
30. Tudor, M.O.; Becker, J.J.; White, P.S.; Gagne, M.R. Diastereoisomer Interconversion in Chiral BiphepPtX_2 Complexes. Organometallics. **2000**, *19*, 4376-4384.
31. Doherty, S.; Knight, J.G.; Hardacre, C.; Lou, H.K.; Newman, C.R.; Rath, R.K.; Campbeil, S.; Nieuwenhuyzen, M. Highly Efficient Asymmetric Hetero-Diels−Alder Reactions of Carbonyl Compounds Catalyzed by Lewis Acid Platinum Complexes of Conformationally Flexible NUPHOS-Type Diphosphines. Organometallics. **2004**, *23*, 6127-6133.
32. Doherty, S.; Newman, C.R.; Rath, R.K.; Nieuwenhuyzen, M.; Knight, J.G. Comparative Study of Diastereoisomer Interconversion in Chiral BINOL-ate and Diamine Platinum Complexes of Conformationally Flexible NUPHOS Diphosphines. Organometallics. **2004**, *23*, 1055-1064.
33. Bovio, B.; Bonati, G.; Banditelli, L. Gaz Chim Ital. **1998**, *115*, 613-618.
34. Bovio, B.; Banditelli, G.; Bandini, L. X-ray crystal Structure of [1,2-bis(diphenylphosphino)ethane]bis(3,5-dimethylpyrazole-N)platinum(II) tetrafluoroborate dichloromethane solvate, [(Ph2PCH2CH2PPh2)Pt(3,4-Me2pzH)2][BF4]2·CH2Cl2. Inorg Chim Acta. **1985**, *96*, 213-223.
35. Jones, R.; Williams, D.J.; Wood, P.T.; Woollins, J.D. The coordination chemistry of silylsulphurdiimides. Polyhedron, **1989**, *8*, 91-96.
36. Baldini, A.L.; Banditelli, G.; Bovio, B. Protonation of platinum(II) pyrazolates: synthesis, characterization and X-ray crystal structure of [Pt(dppe)(Hpz-N)2][BF4]2·CHCl3·H2O (Hpz-N=unsubstituted pyrazole). Polyhedron. **2001**, *20*, 2869-2875.
37. Stang, P.J.; Olenyuk, B.; Arif, A.M. Diastereomeric Square-Planar Platinum(II) and Palladium(II) Complexes Due to Restricted Rotation about the Chelated M-N Heteroaryl Bond. Organometallics. **1995**, *14*, 5281-5289.
38. Stang, P.J.; Cao, D.H. Transition Metal Based Cationic Molecular Boxes. Self-Assembly of Macrocyclic Platinum(II) and Palladium(II) Tetranuclear Complexes. J Am Chem Soc. **1994**, *116*, 4981-4982.; Stang, P.J.; Cao, D.H.; Saito, S.; Arif, A.M. Self-Assembly of Cationic, Tetranuclear, Pt(II) and Pd(II) Macrocyclic

Squares. x-ray Crystal Structure of [Pt^{2+}(dppp)(4,4'-bipyridyl).cntdot.2-OSO$_2$CF$_3$]$_4$. J Am Chem Soc. **1995**, *117*, 6273-6283.

39. Weilandt, T.; Low, N.L.; Schnakenburg, G.; Daniels, J.; Nieger, M.; Schailey, C.A.; Lutzert, A. Exploring the Palladium- and Platinum-Bis(pyridine) Complex Motif by NMR Spectroscopy, X-ray Crystallography, (Tandem) Mass Spectrometry, and Isothermal Titration Calorimetry: Do Substituent Effects Follow Chemical Intuition?. Chem Eur J. 2012, *18*, 16665-16676.
40. Xu, X.; James, S.L.; Mingos, D.M.P.; White, A.J.P.; Williams, P.J. Platinum(II) phosphine and orotate complexes with aminopyridine co-ligands, and their molecular recognition *via* hydrogen bonding. J Chem Soc, Dalton Trans. **2000**, 3783-3790.
41. Lu, N.; Norman, N.C.; Orpen, A.G.; Quayle, M.J.; Timms, P.L.; Whitell, G.R. Transition metal complexes incorporating the BF$_2$ ligand formed by oxidative addition of the B–B bond in B$_2$F$_4$. J Chem Soc, Dalton Trans. **2000**, 4032-4037.
42. DePriest, J.; Zheng, G.Y.; Goswami, N.; Eichhom, DM.; Woods, C.; Rilema, D.P. Structure, Physical, and Photophysical Properties of Platinum(II) Complexes Containing Bidentate Aromatic and Bis(diphenylphosphino)methane as Ligands. Inorg Chem. **2000**, *39*, 1955-1963.
43. Becker, J.J.; White, P.S.; Gagne, M.R. Synthesis and Characterization of Chiral Platinum(II) Sulfonamides: (dppe)Pt(NN) and (dppe)Pt(NO) Complexes. Inorg Chem. **1999**, *38*, 798-801.
44. Obehauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Langes, C.; Rieder, A.; Brüggeller, P. Nickel(II), palladium(II), platinum(II) and platinum(IV) complexes of cis-1,2-bis(diphenylphosphino) ethene and nitrogen-containing heterocycles or sulfur ligands. Inorg Chim Acta.**1998**, *274*, 143-154.
45. Peng, Y.L.; Lai, S.L.; Lin, Ch.Ch. Preparation of Polypeptide via Living Polymerization of *Z*-Lys-NCA Initiated by Platinum Complexes. Macromolecules, **2008**, *41*, 3455-3459.
46. Becker, J.J.; White, P.S.; Gagne, M.R. Asymmetric Catalysis with the Normally Unresolvable, Conformationally Dynamic 2,2‘-Bis(diphenylphosphino)-1,1‘-biphenyl (Biphep). J Am Chem Soc. **2001**, *123*, 9478-9479.
47. Doherty, S.; Goodrich, P.; Hardacre, C.; Luo, H.K.; Neuwenhuyzen, M.; Rath, R.K. Lewis Acid Platinum Complexes of Conformationally Flexible NUPHOS Diphosphines: Highly Efficient Catalysts for the Carbonyl−Ene Reaction. Organometallics. **2005**, *24*, 5945-5955.
48. Doherty, S.; Newman, C.R.; Rath, R.K.; van den Berg, J.A.; Handacre, C.; Neuwenhuyzen, M.; Knight, J.G. Comparative Study of Diastereoisomer Interconversion in Chiral BINOL-ate and Diamine Platinum Complexes of Conformationally Flexible NUPHOS Diphosphines. Organometallics. **2004**, *23*, 1055-1064.
49. Browing, C.S.; Farrar, D.H.; Frankel, D.C. Structures of Pd[(PPh$_2$)$_2$(NMe)]Cl$_2$, Pt[(PPh$_2$)$_2$(NMe)]Cl$_2$ and Pt[(PPh$_2$)$_2$(NMe)](CN)$_2$. Acta Crystallogr Sect C. **1992**, *48*, 806-811.
50. Pawlowski, V.; Kunkely, H.; Lennartz, C.; Bohn, K.; Vogler, A. Synthesis, Structure, Optical Properties and Theoretical Studies of Pt(P−P)(CN)2 with P−P = 1,2-Bis(diphenylphosphanyl)benzene and 2,2′-Bis(diphenylphosphanyl)-1,1′-binaphthyl − Luminescence from Metal-to-Ligand Charge Transfer and Intraligand States. Eur J Inorg Chem. 2004, 4242-4246.
51. Stickel, M.; Maichle-Maessmer, C.; Wesemann, L.; Meyer, H.A. Bis(phosphinomethyl)phenylamines and bis(phosphinomethyl)sulfides and their reaction with d8-platinum group precursors. Polyhedron. **2012**, *46*, 95-104; Polyhedron. **2013**, *52*, 1471-1480.
52. Braumschweig, H.; Damme, A.; Kupfer, T. Conversion of trans-Diboran(4)yl Platinum Complexes into Their cis-Bisboryl Analogues. Chem Eur J. 2013, *19*, 14682-14686.
53. Lesley, G.; Nguyen, P.; Taylor, N.J.; Marder, T.B.; Scott, A.J.; Clegg, W.; Norman, N.C. Synthesis and Characterization of Platinum(II)−Bis(boryl) Catalyst Precursors for Diboration of Alkynes and Diynes: Molecular Structures of *cis*-[(PPh$_3$)$_2$Pt(B-4-Bu^{t}cat)$_2$], *cis*-[(PPh$_3$)$_2$Pt(Bcat)$_2$], *cis*-[(dppe)Pt(Bcat)$_2$], *cis*-[(dppb)Pt(Bcat)$_2$], (*E*)-(4-MeOC$_6$H$_4$)C(Bcat)=CH(Bcat), (*Z*)-(C$_6$H$_5$)C(Bcat)=C(C$_6$H$_5$)(Bcat), and (*Z*,*Z*)-(4-MeOC$_6$H$_4$)C(Bcat)=C(Bcat)C(Bcat)=C(4-MeOC$_6$H$_4$)(Bcat) (cat = 1,2-O$_2$C$_6$H$_4$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dppb = Ph$_2$P(CH$_2$)$_4$PPh$_2$). Organometallics. **1996**, *15*, 5137-5154.