

Review

Organophosphines in Cis-PtP₂CCl Derivatives Structural Aspects

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Abstract: This manuscript summarizes and analyzes X-ray data of monomeric cis-PtP₂CCl derivatives. These complexes crystallize in the following crystal systems: tetragonal, P4₂/n (3), triclinic, P\bar{1} (10), orthorhombic, P2₁2₁2₁ (prevails)(16), and monoclinic, P2₁/c (prevails) (36) examples. There are three sub-groups of the respective complexes: Pt(η¹-PL)₂(η¹-CL)(η¹-Cl); Pt(η²-P₂L)(η¹-CL)(η¹-Cl) and Pt(η¹-PL)(η²-P,CL)(η¹-Cl). The chelating P,P-donor ligands form: four-(POP, PCP), five-(PC₂P), six-(PC₃P, PCNCP), seven-(PC₄P) and even ten-(PCNCNCNCP) membered rings. The chelating P,C-donor ligands create three-(PC), four-(PCC) and five-(PC₂C) membered rings. The mean Pt-L bond distance elongates in the sequence: 2.10 Å (C, trans to P) < 2.222 Å (P, trans to Cl) < 2.312 Å (P, trans to C) < 2.360 Å (Cl, trans to P). There are examples which exist in two isomeric forms, of the distortion isomer type.

Keywords: structures; cis-PtP₂CCl; trans-influence; isomer

1. Introduction

Organophosphines ligands are very attractive and useful in the chemistry of platinum [1]. There are several hundred organoplatinum complexes which were studied by the X-ray method. Structural data of organoplatinum complexes of the types cis-PtP₂C₂ [2], PtPC₃ and PtP₂CX (X = H, F or OL) [3], and PtP₂CX (X = N/L or BL) [4] we reviewed.

The aim of this manuscript is to classify and analyze structural data of cis-PtP₂CCl derivatives. The structures are arranged in the sequence of increasing number of atoms in the respective metallocyclic rings.

2. Cis-PtP₂CCl Derivatives

There are over sixty examples of this coordination sphere for which structural parameters are available. These complexes from a coordination mode of the respective ligands viewpoint are divided into the three sub-groups: Pt(η¹-PL)₂(η¹-CL)(η¹-Cl), Pt(η²-P₂L)(η¹-CL)(η¹-Cl) and Pt(η¹-PL)(η²-P,CL)(η¹-Cl).

2.1. Cis-Pt(η¹-PL)₂(η¹-CL)(η¹-Cl)

In seventeen examples, only monodentate ligands form cis-configurations with an inner coordination sphere of PtP₂CCl type. These are mostly colorless or yellow, and crystallize in three crystal systems: triclinic (3), orthorhombic (5) and monoclinic (9) examples. Such complexes are: [Pt(PMe₃)₂{η¹-C₈H₅BN(SiMe₃)₂}(Cl)] [5], [Pt(PEt₃)₂{η¹-C₅H₂Ph₂}(Cl)] [6], [Pt(PEt₃)₂(Et)(Cl)] [7],

[Pt(PEt₃)₂(C₆F₅)(Cl)] [8], [Pt(PEt₃)₂{η¹-C(SMe)=CHPh}(Cl)] [9], [Pt(PPh₃)₂{η¹-F₂C=CC(Cl)(F₂)}(Cl)] [10], [Pt(PPh₃)₂(CH₂PPh₃)(Cl)]CH₂Cl₂ [11,12], [Pt(PPh₃)₂{CH₂C(O)CH₂Cl}(Cl)] [13], [Pt(PPh₃)₂{η¹-C₆H₄OPh}(Cl)] [14], [Pt(PPh₃)₂{η¹-C₈H₁₅N₂}(Cl)]BF₄.CH₂Cl₂ [15], [Pt(PPh₃)₂{η¹-C₁₁H₁₉N₂}(Cl)]BF₄.CH₂Cl₂ [15], [Pt(PPh₃)₂{η¹-C₁₀H₁₁ClN₂SSi}(Cl)]C₄H₈O [16], [Pt(PPh₃)₂{η¹-C₈H₁₂N₂}(Cl)]BF₄ [17], [Pt{P(H)Mes₂}₂t(Me)(Cl)] [18], [Pt(Ph₂PC≡CPh)₂(Me)(Cl)].0.5CH₂Cl₂ [19], [Pt{P(NC₅H₄OS)Ph₂}₂(Me)(Cl)]CHCl₃ [20], and [Pt{P(η²-C₇H₅NO)Ph₂}(Me)(Cl)]PrⁱOH [21]. The structure of [Pt(PPh₃)₂{η¹-C₈H₁₂N₂}(Cl)]⁺ [17] is shown in Figure 1 as an example.

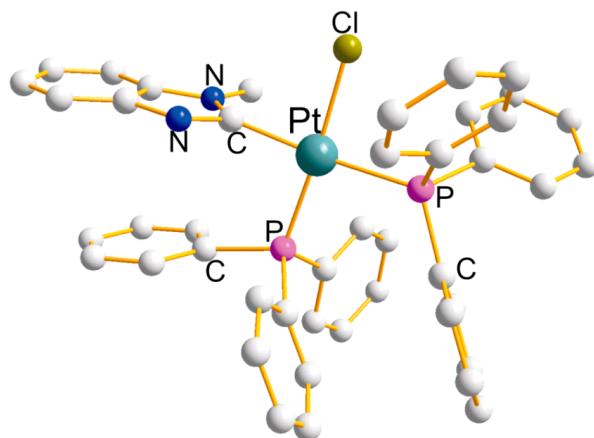


Figure 1. Structure of [Pt(PPh₃)₂{η¹-C₈H₁₂N₂}(Cl)]⁺ [17].

The mean Pt-L bond distance elongates in the order: 2.086 Å (C, trans to P) < 2.234 Å (P, trans to Cl) < 2.340 Å (P, trans to C) < 2.370 Å (Cl, trans to P). The cis-L-Pt-L bond angles (mean values) open in the sequence: 85.5° (C-Pt-Cl), (Cl-Pt-P) < 90.3° (C-Pt-P) < 98.9° (P-Pt-P). The mean values of trans-L-Pt-L bond angles are 169.5° (C-Pt-P) and 174.5° (Cl-Pt-P). The sum of all four bond distances (Pt-P(x2) + Pt-C + Pt-Cl) is 9.03 Å.

2.2. Cis-Pt(η²-P₂L)(η¹-CL)(η¹-Cl)

There are over forty such complexes which crystallize in four crystal systems: tetragonal (3), triclinic (6), orthorhombic (9) and monoclinic (24) examples. The structures are arranged in the order of increasing number of atoms in the respective metallocycle. In three complexes: [Pt(η²-POPL){η¹-C(Cl)=CCl₂}(Cl)] [22], [Pt{η²-Ph₂PCH₂PPh₂}(C₆F₅)(Cl)] [23] and [Pt{η²-Bu^t₂PCH₂PBu^t₂}(η¹-C₈H₃F₆)(Cl)] [24] each chelating-P,P donor ligand forms a four-membered metallocyclic ring with values of the P-Pt-P bite angles of 70.6° (POP) [22] and 73.8° (PCP) (mean) [23,24].

In another twenty five complexes: [Pt{η²Ph₂PCH=CHPPh₂}(CF₃)(Cl)] [25], [Pt{η²-Ph₂PCH=CHPPh₂}(η¹-allyl)(Cl)] [26], [Pt{η²-Me₂P(CH₂)₂PM₂}(C₆F₅)(Cl)]CH₂Cl₂ [27], [Pt{η²-Prⁱ₂P(CH₂)₂PPrⁱ₂}(Ph)(Cl)] [28], [Pt{η²-Ph₂P(CH₂)₂PPh₂}(C₆F₅)(Cl)]pyridine [29], [Pt{η²-Ph₂P(CH₂)₂PPh₂}(η¹-COC₃F₇)(Cl)] [30], [Pt{η²-Ph₂P(CH₂)₂PPh₂}(η¹-COCOPh)(Cl)] [31], [Pt{η²-Ph₂P(CH₂)₂PPh₂}(η¹-C₇H₁₃O₂)(Cl)]CH₂Cl₂ [32], [Pt{η²-cy₂P(CH₂)₂Pcy₂}{η¹-C₃H₄PPh₂}(Cl)] [33], [Pt{η²-Ph₂PCH₂(Me)CH₂(Me)PPh₂}(Ph)(Cl)] [34], [Ph{η²-Ph₂PCH₂(Me)CH₂(Me)PPh₂}{η¹-C₂H₆ClO₂}(Cl)] [35], [Pt{η²-Ph₂P(CH₂(Me)CH₂(Me)PPh₂){η¹-CHClSiMe₃}(Cl)]Et₂O [36], [Pt{η²-cppc}{η¹-neopentyl}(Cl)]Me₂CO [37], [Pt{η²-(CH₂)₄C(CH₂O)₂P(CH₂)₂P(OCH₂)₂C(CH₂)₄}{η¹-neopentyl}(Cl)]CH₂Cl₂ [38], [Pt{η²-Ph₂P(η²-C₅H₈)PPh₂}{η¹-neopentyl}(Cl)] [39], [Pt{η²-(C₅H₁₀N)₂P(η²-C₅H₈)P(NC₅H₁₀)₂}(Me)(Cl)] [39], [Pt{η²-C₅H₁₀N)₂P(η²-C₅H₈)P(NC₅H₁₀)₂}{η¹-neopentyl}(Cl)] [39], [Pt{η²-(PhO)₂P(η²-C₅H₈)P(OPh)₂}{η¹-neopentyl}(Cl)] [39], [Pt{η²-(η²-C₆H₁₂)P(CH₂)₂P(η²-C₆H₁₂)}(Ph)(Cl)] [40], [Pt{η²-(η²-C₆H₁₂)P(CH₂)₂P(η²-C₆H₁₂)}(Me)(Cl)] [40], [Pt{η²-(η²-C₁₀H₂₀)P(η²-C₆H₄)P(η²-C₁₀H₂₀)}(Me)(Cl)]CH₂Cl₂ [40], [Pt{η²-(η²-C₁₆H₁₆)P(CH₂)₂P(η²-C₁₆H₁₆)}(Ph)(Cl)]CHCl₃ [40], [Pt{η²-(η²-C₆H₁₂)P(η²-C₆H₄)P(η²-C₆H₁₂)}(Me)(Cl)] (Figure 2) [41], and

$[\text{Pt}\{\eta^2\text{-C}_6\text{H}_{12}\}\text{P}(\eta^2\text{-C}_6\text{H}_4)\text{P}(\eta^2\text{-C}_6\text{H}_{12})](\text{Ph})(\text{Cl})$] [42], each chelating-P,P ligand creates a five-membered metallocyclic ring with a mean P-Pt-P bite angle of 86.2° (PC_2P).

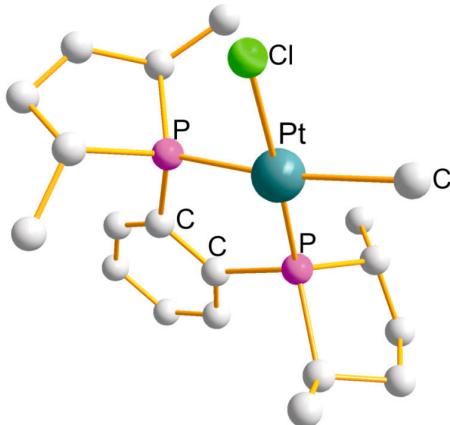


Figure 2. Structure of $[\text{Pt}\{\eta^2\text{-}(\eta^2\text{-C}_6\text{H}_{12})\text{P}(\eta^2\text{-C}_6\text{H}_4)\text{P}(\eta^2\text{-C}_6\text{H}_{12})\}\text{(Me)}(\text{Cl})]$ [40].

In nine complexes: $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}(\text{C}_6\text{F}_5)(\text{Cl})]$ [29], $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}\{\eta^1\text{-C(H)}(\text{Cl})\text{SiMe}_3\}(\text{Cl})]$ [43,44], $[\text{Pt}\{\eta^2\text{-C}_{12}\text{H}_4\text{F}_{13}\}_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_{12}\text{H}_4\text{F}_{13})_2\}\text{(Me)}(\text{Cl})]$ [45], $[\text{Pt}\{\eta^2\text{-Bu}^t_2\text{P}(\eta^2\text{-C}_7\text{H}_6)\text{PBu}^t_2\}\text{(Me)}(\text{Cl})]$ [46], $[\text{Pt}\{\eta^2\text{-Bu}^t_2\text{P}(\eta^2\text{-C}_7\text{H}_6)\text{PPh}_2\}\text{(Me)}(\text{Cl})]$ [46], $[\text{Pt}\{\eta^2\text{-Bu}^t_2\text{P}(\eta^2\text{-C}_7\text{H}_6)\text{P(o-tolyl)}_2\}\text{(Me)}(\text{Cl})]$ [46], $[\text{Pt}\{\eta^2\text{-Bu}^t_2\text{P}(\eta^2\text{-C}_7\text{H}_6)\text{P}(\eta^2\text{-C}_{10}\text{H}_{16}\text{O}_3)\}\text{(Me)}(\text{Cl})]$ [46], $[\text{Pt}\{\eta^2\text{-}(\eta^2\text{-C}_{10}\text{H}_{16}\text{O}_3)\text{P}(\eta^2\text{-C}_7\text{H}_6)\text{P}(\eta^2\text{-C}_{10}\text{H}_{16}\text{O}_3)\}\text{(Me)}(\text{Cl})]\text{CH}_2\text{Cl}_2$ [46], and $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\eta^2\text{-C}_{10}\text{H}_{14}\text{N}_6)\text{PPh}_2\}\text{(Me)}(\text{Cl})]\text{hexane}$ [47] each chelating-P,P ligand creates a six-membered metallocyclic ring with values of the P-Pt-P bite angles of 94° (PC_3P) [29,43–46] and 91.5° (PCNCP) [47].

There are four complexes: $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\eta^2\text{-C}_4\text{H}_8)\text{PPh}_2\}(\text{C}_6\text{F}_5)(\text{Cl})]\text{Me}_2\text{CO}$ (2 isomers) [29], $[\text{Pt}\{\eta^2\text{-diop}\}\{\eta^1\text{-C(H)}(\text{Cl})\text{CO}_2\text{Et}\}(\text{Cl})]$ [48,49] and $[\text{Pt}\{\eta^2\text{-diop}\}\{\eta^1\text{-C(H)}(\text{Me})\text{CO}_2\text{Et}\}(\text{Cl})]$ [50,51] in which each chelating-P,P ligand creates a seven-membered metallocyclic ring with mean P-Pt-P bite angle of 98.2° (PC_4P).

In orthorhombic $[\text{Pt}\{\eta^2\text{-Ph}_2\text{P}(\eta^2\text{-C}_{21}\text{H}_{21}\text{N}_3)\text{PPh}_2\}\text{(Me)}(\text{Cl})]$ [52] the chelating-P,P ligand forms a ten-membered metallocyclic ring, 99° (PCNCNCNCP).

The size of the respective metallocyclic rings influences the Pt-L bond distances. The Pt-L bond distances (mean values) elongates in the sequences:

- four-membered: 1.98 \AA (C, trans to P) $< 2.227 \text{ \AA}$ (P, trans to Cl) $< 2.295 \text{ \AA}$ (P, trans to C) $< 2.365 \text{ \AA}$ (Cl, trans to P);
- five-membered: 2.11 \AA (C, trans to P) $< 2.207 \text{ \AA}$ (P, trans to Cl) $< 2.295 \text{ \AA}$ (P, trans to C) $< 2.360 \text{ \AA}$ (Cl, trans to P);
- six-membered: 2.105 \AA (C, trans to P) $< 2.232 \text{ \AA}$ (P, trans to Cl) $< 2.318 \text{ \AA}$ (P, trans to C) $< 2.360 \text{ \AA}$ (Cl, trans to P);
- seven-membered: 2.14 \AA (C, trans to P) $< 2.230 \text{ \AA}$ (P, trans to Cl) $< 2.326 \text{ \AA}$ (P, trans to C) $< 2.362 \text{ \AA}$ (Cl, trans to P).

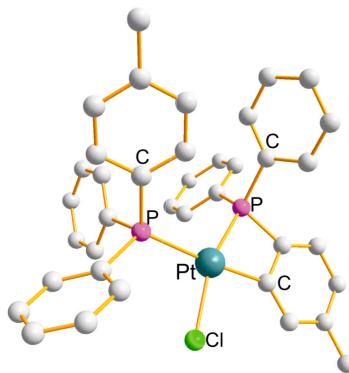
There is a cooperative effect between structural parameters, For example, P-Pt-P bite angles, sum of all four ($\text{Pt-P(x2)} + \text{Pt-C} + \text{Pt-Cl}$) bond distances, remaining cis-L-Pt-L bond angles and trans-L-Pt-L bond angles. When the P-Pt-P bite angle opens, the sum of Pt-L bond distance increases, and the remaining cis-L-Pt-L as well as trans-L-Pt-L bond angles closes: as can be seen from the respective mean values (Table 1).

Table 1. Selected structural parameters of Cis-Pt(η^2 -P₂L)(η^1 -CL)(η^1 -Cl).

Ring (Size)	Pt-L(x4) (Å)	P-Pt-P (°)	Cis-L-Pt-L (°)	Trans-L-Pt-L (°)
four	8.87	72.2	95.8	178
five	8.98	86.1	91.3	175.8
six	9.01	94.0	88.4	173.5
seven	9.03	98.2	87.3	171.8

2.3. Cis-Pt(η^1 -PL)(η^2 -P,CL)(η^1 -Cl)

There are three of these complexes: monoclinic [Pt(PPh₃) $\{\eta^2$ -C₂₄H₃₂PSi₂{(Cl)]} [53], triclinic [Pt{P(p-tolyl)Ph₂} $\{\eta^2$ -C₁₉H₁₆P}{(Cl)]benzene (Figure 3) [54] and orthorhombic [Pt(PMe₃) $\{\eta^2$ -tbtpb]{(Cl)]} [55]. Each chelating-P,C ligand forms a metallocyclic ring: in the [53] first example a three-membered 41° (PC) ring. In the second [54] a four-membered 69.8° (PCC) ring, and in the third [55] a five-membered, 82.6° (PC₂C) ring. The mean Pt-L bond distances elongate in the order: 2.225 Å (trans to Cl) < 2.25 Å (C, trans to P) < 2.27 Å (P, trans to P) < 2.41 (Cl, trans to P).

**Figure 3.** Structure of [Pt{P(p-tolyl)Ph₂} $\{\eta^2$ -C₁₉H₁₆P](Cl)] [54].

3. Conclusions

This manuscript covers over sixty complexes with cis-PtP₂CCl inner coordination sphere. These complexes, from the viewpoint of the coordination mode of the ligands, are divided into the three groups:

- Pt(η^1 -PL)₂(η^1 -CL)(η^1 -Cl) (17 examples);
- Pt(η^2 -P₂L)(η^1 -CL)(η^1 -Cl) (43 examples);
- Pt(η^1 -PL)(η^2 -P,CL)(η^1 -Cl) (3 examples).

The chelating ligands cover a wide variety of metallocyclic rings and the effect of both electronic and steric factors can be seen from the values of the L-Pt-L bite angles. The L-Pt-L bite angles open in the sequence (mean values): 41° (PC) < 69.8° (PCC) < 70.6° (POP) < 73.8° (PCP) < 82.6° (PC₂P) < 91.5° (PCNCP) < 94° (PC₃P) < 98.2° (PC₄P) < 99° (PCNCNCNCP).

The mean Pt-L bond distances elongate in the order: 2.100 Å (C trans to P) < 2.222 Å (P, trans to Cl) < 2.312 Å (P, trans to C) < 2.366 Å (Cl, trans to P).

There are two monoclinic, cis-[Pt(η^2 -Ph₂P(η^2 -C₄H₈))PPh₂} $\{\text{C}_6\text{F}_5\}$ (Cl)]Me₂CO complexes [29] which exist in two isomeric forms. These isomers differ mostly by degree of distortion and are classical examples of distortion isomerism [56–58].

This manuscript together with its precursors [3,4] which classified and analyzed structural data of PtP₂CX (X = H, F or O) [3] and PtP₂CX (X = N or Br) [4], the predominant square planar configuration about the platinum atom is cis rather than trans. The total mean values of Pt-L bond distances in the series of cis-PtP₂CX (X = H, F, O, N or Cl) complexes elongate in the order:

- Pt-P (trans to X): 2.214 Å (O) < 2.220 Å (F) < 2.222 Å (Cl) < 2.240 Å (N) < 2.300 Å (C) < 2.323 Å (H);
- Pt-X (trans to P): 1.65 Å (H) < 2.02 Å (F) < 2.07 Å (N) < 2.075 Å (O) < 2.222 Å (Cl)

As can be seen, the Pt-L bond distances reflect the trans-influence of the respective donor atom. In these series of complexes with cis-configuration, the sum of all four (Pt-P(x2) + Pt-C + Pt-X) bond distances increase with the covalent radius of X atom in the sequence: 8.28 Å (H, 0.30 Å) < 8.54 Å (F, 0.58 Å) < 8.68 Å (O, 0.66 Å) < 8.70 Å (N, 0.70 Å) < 9.00 Å (Cl, 1.00 Å), as would be expected.

Noticeably, the sum of all four Pt-L bond distances, cis- and trans-PtP₂CCl of 9.00 Å versus 8.95 Å, indicates that the complexes with cis-configuration are somewhat less crowded and more distorted than their trans-partners. In the complexes with cis-configuration the Pt-L bonds are more polar and presumably weaker than those in the complexes with trans-configuration, in which the Pt-L bonds are less polar and presumably stronger.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Bu ^t ₂ P(η ² -C ₇ H ₆)PBu ^t ₂	di-t-butyl(2-di-t-butylphosphino)benzyl)phosphine
C ₂ H ₆ ClO ₂	chloro(methoxycarbonyl)methyl
C ₃ H ₄ PPh ₂	1-(diphenylphosphino)propenyl
C ₄ H ₈ O	tetrahydrofuran
C ₅ H ₂ Ph ₂	2-(2,3-diphenylcycloprop-2-en-1-yl)vinyl
(C ₅ H ₁₀ N) ₂ P(η ² -C ₅ H ₈)P(NC ₅ H ₁₀) ₂	1,2-bis(bis(piperidin-1-yl)phosphorino)cyclopentane
(η ² -C ₆ H ₁₂)P(CH ₂) ₂ P(η ² -C ₆ H ₁₂)	1,1'-ethane-1,2-diylbis(2,5-dimethylphospholane)
(η ² -C ₆ H ₁₂)P(η ² -C ₆ H ₄)P(η ² -C ₆ H ₁₂)	1,2-bis((hexa-2,5-diyl)phosphino)benzene
C ₇ H ₁₃ O ₂	1-(tert-butoxycarbinol)ethyl
C ₈ H ₁₂ N ₂	1-methylbenzimidazol-2-ylidene
C ₈ H ₁₅ N ₂	3-((dimethylamino)methylene)-1-methylpyrrolidin-2-ylidene
C ₈ H ₃ F ₆	2,5-bis(trifluoromethyl)phenyl
C ₈ H ₅ BN(SiMe ₃) ₂	1-(bis(trimethylsilyl)amino)-3-phenyl-1H-borizene-2-yl
(η ² -C ₁₀ H ₁₆ O ₃)P(η ² -C ₇ H ₆)P(η ² -C ₁₀ H ₁₆ O ₃)	bis(1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphatricyclo[3.3.1.1 ^{3,7}]dec-8-yl)benzyl
(η ² -C ₁₀ H ₂₀)P(η ² -C ₆ H ₄)P(η ² -C ₁₀ H ₂₀)	1,1'-(1,2-phenylene)bis(2,5-diisopropylphospholane)
C ₁₀ H ₁₁ ClN ₂ SSi	1-(chloro(phenyl)sulfidosilyl)-3-methylimidazolin-2-ylidene
C ₁₁ H ₁₉ N ₂	2,5-bis((dimethylamino)methylene)cyclopentylidene
(C ₁₂ H ₄ F ₁₃) ₂ P(CH ₂) ₃ P(C ₁₂ H ₄ F ₁₃) ₂	propane-1,3-diyl(bis(4-tridecafluoroethyl)phenyl)
(η ² -C ₁₆ H ₁₆)P(CH ₂) ₂ (η ² -C ₁₆ H ₁₆)	1,1'-ethane-1,2-diylbis(2,5-diphenylphospholane)
η ² -C ₁₉ H ₁₆ P	2-(diphenylphosphino)-5-methylphenyl
η ² -C ₂₄ H ₃₂ PSi ₂	1-methyl-2,6-bis(trimethylsilyl)-3,5-diphenylphosphinine
cpc	1-[chloro(piperidin-1-yl)phosphino]-2-[bis(piperidin-1-yl)phosphino]cyclopentane
diop	Ph ₂ PCH ₂ CHOC(H ₂)COCHCH ₂ PPh ₂
P(NC ₅ H ₄ OS)Ph ₂	2-(diphenylphosphino)-2-thienylcarboxamide
P(η ² -C ₇ H ₅ NO)Ph	3-phenyl-1,3-dihydro-2H-1,3-benzaphosphol-2-one
Ph ₂ P(η ² -C ₁₀ H ₁₄ N ₂)PPh ₂	(3-(adenin-9-yl)propyl)bi(diphenylphosphinomethyl) amine
Ph ₂ P(η ² -C ₂₁ H ₂₁ N ₃)PPh ₂	N,N'-dibenzyl-N,N'-bis((diphenylphosphino)methyl)pyridine-2,6-diamine
Ph ₂ P(η ² -C ₅ H ₈)PPh ₂	1,2-bis(diphenylphosphino)cyclopentane
Ph ₂ PCH ₂ (Me)CH ₂ (Me)PPh ₂	2,3-bis(diphenylphosphino)butane
POP	N,N',N'',N'''-tetra-tert-butyl-N,N''-bis(trimethylsilyl)tetraamidotiphosphite
tbtpb	2,4,6-Tri-t-butyl-2,4-dihydro-5-hydroxy-1,3-di-oxo-1,3,5-triphosphabenzene-P,C

References

- Melník, M.; Mikuš, P. Organophosphines in organoplatinum complexes structural aspects of PtPC₃ and PtP₂CX (X = H, F or OL) derivatives. *J. Organomet. Chem.* **2016**, *811*, 1–7. [[CrossRef](#)]
- Melník, M.; Mikuš, P. Organophosphines in organoplatinum complexes: Structural aspects of PtP₂CX (X = NL or BL) derivatives. *J. Organomet. Chem.* **2016**, *813*, 78–83. [[CrossRef](#)]
- Melník, M.; Mikuš, P. Organophosphines in organoplatinum complexes—Structural aspects of trans-PtP₂CCl derivatives. *J. Organomet. Chem.* **2016**, *819*, 46–52. [[CrossRef](#)]
- Melník, M.; Mikuš, P. Organophosphines in organoplatinum complexes—Structural aspects OF PtP₂CX (X = Br or I) derivatives. *J. Organomet. Chem.* **2016**, *823*, 97–102. [[CrossRef](#)]
- Braunschweig, H.; Ye, Q.; Radacki, K. Borylene-based functionalization of Pt-alkynyl complexes by photochemical borylene transfer from [(OC)₅Cr=BN(SiMe₃)₂]. *Chem. Commun.* **2009**, 6979–6981. [[CrossRef](#)] [[PubMed](#)]
- Jacob, V.; Weakley, T.J.R.; Haley, M.M. Rearrangement of a σ-2-(Cycloprop-2-enyl)vinyl- to an η³-Cyclopentadienylplatinum(II) Complex. Selective Protonolysis of the Platinum–Methyl Bond. *Organometallics* **2002**, *21*, 5394–5401. [[CrossRef](#)]
- Bardi, R.; Del Pra, A.; Piazzesi, A.M.; Minniti, D.; Romeo, R. Crystal and Molecular Structure of di(triethylphosphino)(ethyl)chloride platinum(II) complex. *Cryst. Struct. Commun.* **1981**, *10*, 333–335.
- Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevato, V.; Romeo, R.; Belluco, U. Crystal and molecular structure of *cis*-chloro-*p*-tolyl-bis(triethylphosphine)platinum(II) and of *cis*-chloroperfluorophenyl-bis(triethylphosphine)platinum(II). *Inorg. Chim. Acta* **1978**, *31*, 171–175. [[CrossRef](#)]
- Stienborn, D.; Becke, S.; Bruhn, C.; Heinemann, F.W. Platin(II)-Komplexe mit schwefelfunktionalisierten Alkenylliganden. *J. Organomet. Chem.* **1998**, *556*, 189–196. [[CrossRef](#)]
- Russell, D.R.; Tucker, P.A. Crystal and molecular structure of *cis*-chloro(3-chloro-1,1,3,3-tetrafluoropropan-2-one)bis(triphenylphosphine)platinum(II). *J. Chem. Soc. Dalton Trans.* **1975**, 2222–2225. [[CrossRef](#)]
- Engelter, C.; Moss, J.R.; Niven, M.L.; Nassimbeni, L.R.; Reid, G. A cationic ylide complex of platinum(ii): Its structure and formation from a chloromethyl-platinum complex. *J. Organomet. Chem.* **1982**, *232*, C78–C80. [[CrossRef](#)]
- Engelter, C.; Moss, J.R.; Nassimbeni, L.R.; Niven, M.L.; Reidaud, G.; Spiers, J.C. Haloalkyl complexes of the transition metals: IV. The formation of a cationic ylide complex of platinum(II) from a chloromethylplatinum(II) complex and the crystal structures of *cis*-[Pt(CH₂PPh₃)X(PPh₃)₂]I (X = Cl or I). *J. Organomet. Chem.* **1986**, *315*, 255–268. [[CrossRef](#)]
- Henderson, W.; Fawcett, J.; Kemmitt, R.D.W.; McKenna, P.; Russell, D.R. Decomposition pathways of platinum(II) complexes containing alkyl and halide ligands investigated by electrospray mass spectrometry. The X-ray crystal structure of *cis*-[PtCl{CH₂C(O)CH₂Cl}(PPh₃)₂]. *Polyhedron* **1997**, *16*, 2455–2463. [[CrossRef](#)]
- Baukova, T.V.; Oleinikova, N.A.; Kuzmina, L.G. Synthesis, structure, and properties of organoplatinum(ii) derivatives of diphenyl ether. *Izv. Akad. Nauk SSSR Ser. Khimia* **1994**, *43*, 1719–1725. [[CrossRef](#)]
- Alcarazo, M.; Radkowski, K.; Goddard, R.; Furstner, A. Metal complexes with carbene ligands stabilized by lateral enamines. *Chem. Commun.* **2011**, *47*, 776–778. [[CrossRef](#)] [[PubMed](#)]
- Brendler, E.; Hill, A.F.; Wagler, J. A Donor-Stabilized Silanethione or a Si-Substituted N-Heterocyclic Platinum. *Chem. Eur. J.* **2008**, *14*, 11300–11304. [[CrossRef](#)] [[PubMed](#)]
- Kosterke, T.; Pape, T.; Hahn, F.E. Synthesis of NHC Complexes by Oxidative Addition of 2-Chloro-N-methylbenzimidazole. *J. Am. Chem. Soc.* **2011**, *133*, 2112–2115. [[CrossRef](#)] [[PubMed](#)]
- Pelczar, E.M.; Nytko, E.A.; Zhuravel, M.A.; Smith, J.M.; Glueck, D.C.; Sommer, R.; Incarvito, C.D.; Rheingold, A.L. Synthesis and structure of platinum and palladium complexes of dimesitylphosphine. *Polyhedron* **2002**, *21*, 2409–2419. [[CrossRef](#)]
- Johnson, D.K.; Rukaschaisirikul, T.; Sun, Y.; Taylor, N.J.; Canty, A.J.; Carty, A.J. Spectroscopic Properties of Inorganic and Organometallic Compounds. *Inorg. Chem.* **1993**, *32*, 5544–5549. [[CrossRef](#)]
- Milton, H.L.; Wheatley, M.V.; Slawin, A.M.Z.; Woollins, J.D. Synthesis and coordination of 2-diphenylphosphinothiophenocarboxamide and bis(2,5-diphenylphosphinepicolinamide). *Polyhedron* **2004**, *23*, 2575–2585. [[CrossRef](#)]

21. Bennett, J.; Doyle, R.J.; Lee, H.Y.; Lu, D.; Salem, G.; Speldewinde, D.J.; Tifan, M.; Willis, A.C. Synthesis of 1,3-azaphosphol-2-ones. Crystal and molecular structures of [SP-4-2]-dichlorobis (3-phenyl-1,3-dihydrobenzo [1,3]azaphosphol-2-one-P)palladium(II) and its chloro(methyl)platinum(II) analogue. *Dalton Trans.* **2010**, *39*, 256–264. [[CrossRef](#)] [[PubMed](#)]
22. Scherer, O.J.; Konrad, R.; Guggolz, E.; Ziegler, M.L. Elementorganische Amin/Imin-Verbindungen, XXIV. Tris[(*tert*-butylimino)[*tert*-butyl(trimethylsilyl)amino]-phosphan]platin(0) – ein wertvoller Synthesebaustein. *Chem. Ber.* **1983**, *116*, 2676–2690. [[CrossRef](#)]
23. Deacon, G.B.; Nelson, K.T.; Tiekkink, E.R.T. [Bis(diphenylphosphino)methane-*P,P'*](chloro)(pentafluorophenyl) platinum(II): PtCl(dppm)C₆F₅. *Acta Crystallogr. Sect. C* **1991**, *47*, 955–957. [[CrossRef](#)]
24. Iverson, C.N.; Lachicotte, R.J.; Muller, C.; Jones, W.D. η^2 -Coordination and C–H Activation of Electron-Poor Arenes. *Organometallics* **2002**, *21*, 5320–5333. [[CrossRef](#)]
25. Del Pra, A.; Zanotti, G.; Prazzesi, A.; Bellucco, U.; Ros, R. The crystal and molecular structure of PtCl(CF₃)(*cis*-Ph₂PCH=CHPPh₂). *Trans. Met. Chem.* **1979**, *4*, 381–384. [[CrossRef](#)]
26. Calligarlie, M.; Carturan, G.; Nardin, G.; Scrivanti, A.; Wojcicki, A. Metal complexes with carbene ligands stabilized by lateral enamines. *Organometallics* **1983**, *2*, 865–874.
27. Hughes, R.P.; Ward, A.J.; Golen, J.A.; Incarvito, C.O.; Rheingold, A.L.; Zakharov, L.N. Synthesis, molecular structures, and chemistry of some new palladium(II) and platinum(II) complexes with pentafluorophenyl ligands. *Dalton Trans.* **2004**, 2720–2727. [[CrossRef](#)] [[PubMed](#)]
28. Schwatz, B.D.; Brennessel, W.W.; Jones, W.D. C–CN vs. C–H Cleavage of Benzonitrile Using [(dippe)PtH]₂. *Organometallics* **2011**, *30*, 1523–1529.
29. Deacon, G.B.; Elliott, P.W.; Erven, A.P.; Meyer, G. The Synthesis by Decarboxylation Reactions and Crystal Structures of 1, n-Bis(diphenylphosphino)alkane(pentafluorophenyl)-platinum(II) Complexes. *Z. Anorg. Allg. Chem.* **2005**, *631*, 843–850. [[CrossRef](#)]
30. Wicht, D.K.; Glueck, D.S.; Liable-Sands, L.M.; Rheingold, A.L. Terminal Platinum(II) Perfluoroacyl Phosphido Complexes: Synthesis and Dynamic Processes. *Organometallics* **1999**, *18*, 5130–5140. [[CrossRef](#)]
31. You, Y.J.; Chen, J.T.; Cheng, M.C.; Wang, Y. Solvent-controlled equilibria of substitution and isomerization of α -ketoacyl complexes of platinum(II). X-ray single-crystal structure of *cis*-Pt(COCOPh)(Cl) (PPh₂CH₂CH₂PPh₂). *Inorg. Chem.* **1991**, *30*, 3621–3625. [[CrossRef](#)]
32. Scriban, C.; Glueck, D.S.; Zakharov, L.N.; Kassel, W.S.; DiPasquale, A.G.; Golen, J.A.; Rheingold, A.L. P–C and C–C Bond Formation by Michael Addition in Platinum-Catalyzed Hydrophosphination and in the Stoichiometric Reactions of Platinum Phosphido Complexes with Activated Alkenes. *Organometallics* **2006**, *25*, 5757–5767. [[CrossRef](#)]
33. Bennett, M.A.; Kwan, L.; Rae, A.D.; Wenger, E.; Willis, A.C. Preparation and reactivity of mononuclear platinum(0) complexes containing a η^2 -coordinated alkynylphosphine. *J. Chem. Soc. Dalton Trans.* **2002**, 226–233. [[CrossRef](#)]
34. Johansson, M.H.; Malmstrom, T.; Wendt, O.F. Chiral platinum(II) complexes. Crystal and molecular structures of *cis*-[PtPhCl(*(R,R)*-CHIRAPHOS)] and *cis*-[PtCl₂(*(R,R)*-CHIRAPHOS)]. *Inorg. Chim. Acta* **2001**, *316*, 149–152. [[CrossRef](#)]
35. Ferguson, G.; Gallagher, J.F.; McAlees, A.J.; McCrindle, P. Mechanism and Stereochemistry of the Reaction of Dichloroplatinum(II) Complexes with Diazo Compounds. X-ray Structures of Four Key Products: [(2*R*,3*R*)-Bis(diphenylphosphino)butane]chloro-[*(S*)-chloro(methoxycarbonyl)methyl]platinum(II), (η^4 -1,5-Cyclooctadiene)[3-chloro-5-(dimethoxyphosphonyl)-2-methoxy-4,1,2-platinaoxaphospholane *P*-oxide],(*R,R*)-[Chloro(dimethoxyphosphonyl)methyl][chloro-(trimethylsilyl)methyl] (1,5-cyclooctadiene) platinum(II), and Chloro[chloro(dimethoxyphosphonyl)methyl](η^4 -1,5-cyclooctadiene)platinum(II). *Organometallics* **1997**, *16*, 1053–1062.
36. Argazzi, R.; Bergamini, P.; Costa, E.; Gee, V.; Hogg, J.K.; Martin, A.; Orpen, A.G.; Pringle, P.G. Anchimeric Assistance by Platinum(II) in the Epimerizations of [PtX(CH₂SiMe₃)*(R,R*-chiraphos)]. *Organometallics* **1996**, *15*, 5591–5597. [[CrossRef](#)]
37. Dahlenburg, L.; Mertel, S. Chiral bisphosphanes. V. Chloro[*rac,trans*-1-[chloro(piperidin-1-yl) phosphino]-2-[bis(piperidin-1-yl)phosphino]cyclopentane-*P,P'*]neopentyplatinum(II) acetone solvate. *Acta. Crystallogr. Sect. C* **1999**, *55*, 347–349. [[CrossRef](#)]

38. Squires, M.E.; Sardella, D.J.; Kool, L.B. C-H Activation by [Bis(dialkoxyphosphino)ethane]platinum(0) and [Bis(diaminophosphino)ethane]platinum(0) Complexes: Platinum-Platinum Dimer Formation Limits Yields. *Organometallics* **1994**, *13*, 2970–2978. [[CrossRef](#)]
39. Dahlenburg, L.; Mertel, S. Chiral chelate phosphanes: XI. Application of cyclopentane-based C_2 chiral bis(phosphane) ligands $C_5H_8(PR_2)_2$ to Pt Sn-catalyzed styrene hydroformylation. *J. Organomet. Chem.* **2001**, *630*, 221–243. [[CrossRef](#)]
40. Quino-o, M.A.; Zureick, A.H.; Blank, N.F.; Anderson, B.J.; Chapp, T.W.; Kim, Y.; Glueck, D.S.; Rheingold, A.L. Synthesis and Structure of Platinum Bis(phospholane) Complexes $Pt(diphos^*)(R)(X)$, Catalyst Precursors for Asymmetric Phosphine Alkylation. *Organometallics* **2012**, *31*, 6900–6910. [[CrossRef](#)]
41. Scriban, C.; Wicht, D.K.; Glueck, D.S.; Zakharov, L.N.; Golen, J.A.; Rheingold, A.L. Platinum(II) Phosphido Complexes as Metalloligands. Structural and Spectroscopic Consequences of Conversion from Terminal to Bridging Coordination. *Organometallics* **2006**, *25*, 3370–3378. [[CrossRef](#)]
42. Brunker, T.J.; Blank, N.F.; Moncarz, J.R.; Scriban, C.; Anderson, B.J.; Glueck, D.S.; Zakharov, L.N.; Golen, J.A.; Sommer, R.D.; Incarvito, C.D. Chiral Palladium(0) *trans*-Stilbene Complexes: Synthesis, Structure, and Oxidative Addition of Phenyl Iodide. *Organometallics* **2005**, *24*, 2730–2746. [[CrossRef](#)]
43. Bergamini, P.; Costa, E.; Sostero, S.; Ganter, C.; Hogg, J.; Orpen, A.G.; Pringle, P.G. The reactions of Me_3SiCHN_2 with $[PtX_2(S,S\text{-skewphos})]$: Highly diastereoselective carbene insertions into Pt Cl bonds, and Me_3SiCHN_2 as a CH_2N_2 equivalent. *J. Organomet. Chem.* **1993**, *455*, C13–C16. [[CrossRef](#)]
44. Bergamini, P.; Costa, E.; Orpen, A.G.; Ganter, C.; Pringle, P.G. Highly stereospecific carbene insertions into platinum-halide bonds. Crystal structure of $[PtCl(S\text{-CHClSiMe}_3)(S,S\text{-Ph}_2PCHMeCH}_2CHMePPh_2)]$. *J. Chem. Soc. Dalton Trans.* **1994**, 651–655. [[CrossRef](#)]
45. Berven, B.M.; Kousantonis, G.A.; Skelton, B.W.; Trengove, R.D.; White, A.H. Highly fluorous complexes of nickel, palladium and platinum: Solubility and catalysis in high pressure CO_2 . *Dalton Trans.* **2011**, 4167–4174. [[CrossRef](#)] [[PubMed](#)]
46. Fanjul, T.; Eastham, G.; Floure, J.; Forrest, S.J.K.; Haddow, M.F.; Hamilton, A.; Pringle, P.G.; Golen, A.G.; Waugh, M. Interplay of bite angle and cone angle effects. A comparison between $o\text{-C}_6H_4(CH_2PR_2)(PR'_2)$ and $o\text{-C}_6H_4(CH_2PR_2)(CH_2PR'_2)$ as ligands for Pd-catalysed ethene hydromethoxycarbonylation *Dalton Trans. Dalton Trans.* **2013**, *42*, 100–115. [[CrossRef](#)] [[PubMed](#)]
47. Zhang, Q.; Hua, G.; Bhattacharyya, P.; Slawin, A.M.Z.; Woollins, J.D. Syntheses and Coordination Chemistry of Aminomethylphosphine Derivatives of Adenine. *Eur. J. Inorg. Chem.* **2003**, 2426–2437. [[CrossRef](#)]
48. Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A.G.; Pringle, P.G. Convenient synthesis of. alpha.-chiral platinum alkyls. *Organometallics* **1991**, *10*, 2989–2990. [[CrossRef](#)]
49. Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A.G.; Pringle, P.G. Diastereoselective carbene insertions into platinum-halogen bonds. Crystal structure of $[PtCl(R\text{-CHClCO}_2Et)(R,R\text{-diop})]$. *Organometallics* **1992**, *11*, 3879–3885. [[CrossRef](#)]
50. Bergamini, P.; Costa, E.; Cramer, D.; Hogg, J.; Orpen, A.G.; Pringle, P.G. Diastereoselective C-C Bond Formation by Carbene Insertions into Pt-CH₃ Bonds. *Organometallics* **1994**, *13*, 1058–1060. [[CrossRef](#)]
51. Bergamini, P.; Costa, E.; Orpen, A.G.; Pringle, P.G.; Smith, M.B. Reactions of Diazo Carbonyls with $[PtX(CH_3)(\text{chiral diphosphine})]$ ($X = Cl, Br, I$): Chemoselectivity and Diastereoselectivity of Pt-C and Pt-X Carbene Insertion. *Organometallics* **1995**, *14*, 3178–3186. [[CrossRef](#)]
52. Wang, Z.J.; Wang, X.X.; Wan, C.Q. Chlorido{ N^2,N^6 -dibenzyl- N^2,N^6 -bis[(diphenylphosphanyl)methyl] pyridine-2,6-diamine}methylplatinum(II). *Acta Crystallogr. Sect. E Struct. Rep. Online* **2010**, *66*, m1341–m1342. [[CrossRef](#)] [[PubMed](#)]
53. Moores, A.; Mezailles, N.; Ricard, L.; Jean, Y.; LeFloch, P. η^2 -Palladium and Platinum(II) Complexes of a λ^4 -Phosphinine Anion: Syntheses, X-ray Crystal Structures, and DFT Calculations. *Organometallics* **2004**, *23*, 2870–2875. [[CrossRef](#)]
54. Bennett, M.A.; Bhargava, S.K.; Priver, S.H.; Willis, A.C. Selective Cleavage by Acids of One Metal–Carbon σ -Bond of a Bis(*ortho*-platinated) Triarylphosphane: A ^{31}P NMR *trans*-Influence Series Based on the Unit $Pt(\kappa^2\text{-C}_6H_3\text{-5-Me-2-PPh}_2)(PPh_2\text{-4-tol})$. *Eur. J. Inorg. Chem.* **2008**, 3467–3483. [[CrossRef](#)]
55. Clendenning, S.B.; Hitchcock, P.B.; Nixon, J.F. First η^1 -ligated 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene complexes and the remarkable trihydration reaction of *trans*-[$PtCl_2(PMe_3)(P_3C_3Bu^t_3)$] to *cis*-[$PtCl(PMe_3)(P_3O_3C_3H_5Bu^t_3)$], containing the novel $CH(Bu^t)PH(O)C(Bu^t)PH(O)CH(Bu^t)P(O)$ ring system. *Chem. Commun.* **1999**, 1377–1381. [[CrossRef](#)]

56. Melník, M. Structural isomerism of copper(II) compounds. *Coord. Chem. Rev.* **1982**, *47*, 239–261. [[CrossRef](#)]
57. Melník, M.; Holloway, C.E. Stereochemistry of platinum coordination compounds. *Coord. Chem. Rev.* **2006**, *250*, 2261–2270. [[CrossRef](#)]
58. Melnik, M.; Mikus, P. Stereoisomers of organoplatinum complexes. *J. Organomet. Chem.* **2015**, *239*, 779–780. [[CrossRef](#)]



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