

Review

Variable Combinations of Tridentate Ligands in $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$ Derivatives: Structural Aspects

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Abstract: This review covers over fifty $\text{Pt}(\text{II})$ monomeric complexes with a wide combination of η^3 -ligands of the composition $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$, ($\text{X}_3 = \text{N}_3; \text{S}_3; \text{Te}_3; \text{ONO}; \text{CNC}; \text{SeNSe}; \text{ONC}; \text{ONS}; \text{CNS}; \text{NNC}; \text{NNS}; \text{NNSe}; \text{SOS}; \text{SBS}; \text{NON}; \text{SSO}$). The η^3 -ligand with monodentate PL displays distorted square-planar geometry about $\text{Pt}(\text{II})$ atoms. The structural parameters (Pt-L , L-Pt-L) are analyzed and discussed, with a particular emphasis on the distortion of square-planar geometry about $\text{Pt}(\text{II})$ atoms, as well as of the trans-influence. There is a relation between the membered nature of the metallocycles and the distortion of square-planar geometry about the $\text{Pt}(\text{II})$ atoms. The distortion increases as indicated by parameter τ_4 in the following order: $0.023 (6+6) < 0.024 ({}^+5) < 0.040 (5+6) < 0.062 (5+5)$.

Keywords: structure; $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$; distortion; trans-effect



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1. Introduction

The chemistry of platinum is particularly important in the areas of catalysis and biochemistry. There are numerous published structural studies on platinum complexes that have been classified and analyzed [1]. The high affinity of platinum(II) ions for phosphorous enables it to bind effectively to organophosphines. Organophosphines as soft P-donor ligands are very useful for building a wide variety of platinum complexes. Recently, we classified and analyzed structural data of monomeric organoplatinum complexes with PtP_3C inner coordination spheres [2]. Another review covers structural data of monomeric $\text{Pt}(\text{II})$ coordination complexes with inner coordination spheres, including PtP_4 , PtP_3X , and PtP_2X_2 , in which P-donor ligands are monodentate organomonophosphines [3].

This study aims to correlate the following structural parameters available for $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$: ($\text{X}_3 = \text{N}^1, \text{N}^2, \text{N}^3; \text{S}^1, \text{S}^2, \text{S}^3; \text{Te}^1, \text{Te}^2, \text{Te}^3; \text{O}^1, \text{N}^1, \text{O}^2; \text{O}^1, \text{N}^1, \text{C}^1; \text{O}^1, \text{N}^1, \text{S}^1; \text{N}^1, \text{N}^2, \text{C}^1; \text{N}^1, \text{N}^2, \text{S}^1; \text{N}^1, \text{N}^2, \text{Se}^1; \text{N}^1, \text{C}^1, \text{N}^2; \text{C}^1, \text{N}^1, \text{C}^2; \text{C}^1, \text{N}^1, \text{S}^1; \text{S}^1, \text{C}^1, \text{S}^2; \text{S}^1, \text{B}^1, \text{S}^2; \text{S}^1, \text{S}^2, \text{O}^1; \text{Se}^1, \text{N}^1, \text{Se}^2$).

2. $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$ Derivatives

There are over fifty examples in which the inner coordination spheres about the $\text{Pt}(\text{II})$ atoms of the $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$ type are formed by variable combinations of donor atoms of tridentate ligands. Each η^3 -ligand creates two metallocyclic rings. The complexes based on membered metallocyclic rings can be divided into four groups.

2.1. 6+6-Membered Metallocyclic Rings

There are only three examples in which a η^3 -ligand creates such rings (Table 1). In $[\text{Pt}(\eta^3\text{-C}_{22}\text{H}_{11}\text{F}_6\text{N}_3\text{O}_2\text{-O}^1, \text{N}^1, \text{O}^2)(\text{PPh}_3)]$ (at 173 K) [4], the η^3 -ligand forms a metallocyclic

ring of the $O^1C_3N^1C_3O^2$ type with common ligating N^1 atoms. The values of the chelate L-Pt-L angles are 90.6° (O^1 -Pt- N^1) and 90.2° (N^1 -Pt- O^2). The $O^1C_2NN^1C_3O^2$ type with the respective chelate angles of 88.2° (O^1 -Pt- N^1) and 90.0° (N^1 -Pt- O^2) was found in $[Pt(\eta^3-C_{14}H_{10}N_2O_3-O^1,N^1,O^2)(PPh_3)]$ (at 150 K) [5]. The remaining L-Pt-L angles open in the following order (mean values): 88.1° (O^2 -Pt-P) < 89.0° (O^1 -Pt-P) < 176.0° (N^1 -Pt-P) < 177.7° (O^1 -Pt- O^2). The monodentate PPh_3 displayed square-planar geometry about each Pt(II) atom. The Pt-L bond distance increased in the following order (mean values): $1.995 \text{ \AA}$ (Pt- O^1 trans to O^2) < $1.996 \text{ \AA}$ (Pt- O^2) < $2.010 \text{ \AA}$ (Pt- N^1) < $2.254 \text{ \AA}$ (Pt-P).

Table 1. Structural data for $Pt(\eta^3-X_3)(Y)$ derivatives. ^a—6+6-membered metallocyclic rings.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c ($\text{\AA}$)	L-Pt-L ^c ($^\circ$)	Ref.
$[Pt(\eta^3-C_{22}H_{11}F_6N_3O_2-O^1,N^1,O^2)(PPh_3)]$ (at 173 K)	Pt $O^1N^1O^2P$ ($O^1C_3N^1C_3O^2$) 0.032	O^1 1.994(2) N^1 2.021(2) O^2 2.004(2) P 2.256(2)	O^1,N^1 90.6 ^d N^1,O^2 90.2 ^d O^1,O^2 179.0 O^1,P 90.6 O^2,P 87.5 N^1,P 177.0 O^1,N^1 88.2 ^d N^1,O^2 90.0 ^d	[4]
$[Pt(\eta^3-C_{14}H_{10}N_2O_3-O^1,N^1,O^2)(PPh_3)]$ (at 150 K)	Pt $O^1N^1O^2P$ ($O^1C_2NN^1C_3O^2$) 0.024	O^1 1.995(2) N^1 2.000(2) O^2 1.988(2) P 2.251(2)	O^1,O^2 176.5 O^1,P 89.0 O^2,P 90.7 N^1,P 175.0 S^1,S^2 87.1(2) ^d S^2,S^3 89.5(2) ^d	[5]
$[Pt\{\eta^3-C_{12}H_{24}S_3-S^1,S^2,S^3\}(PPh_3)]BF_4$	Pt $S^1S^2S^3P$ ($S^1C_3S^2C_3S^3$) 0.035	S^1 2.330(2) S^2 2.339(2) S^3 2.336(2) P 2.332(2)	S^1,S^3 176.3(2) S^1,P 91.1(2) S^3,P 92.3(1) S^2,P 171.0(2)	[6]

(^a) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. (^b) Parameter τ_4 , degree of distortion. (^c) The chemical identity of the coordinated atom/ligand is specific to these columns. (^d) Six-membered metallocyclic ring.

For the complex $[Pt\{\eta^3-C_{12}H_{24}S_3-S^1,S^2,S^3\}(PPh_3)]BF_4$, the η^3 -ligand creates a pair of six-membered metallocyclic rings of the $S^1C_3S^2C_3S^3$ type (as shown in Figure 1) [6]. The values of the chelate angles are 87.1° (S^1 -Pt- S^2) and 89.5° (S^2 -Pt- S^3). The remaining L-Pt-L bond angles open in the following order: 91.1° (S^1 -Pt-P) < 92.3° (S^3 -Pt-P) < 171.0° (S^2 -Pt-P) < 176.3° (S^1 -Pt- S^3). The Pt-L bond distance increases in the following order: $2.330 \text{ \AA}$ (Pt- S^1) < $2.332 \text{ \AA}$ (Pt-P) < $2.336 \text{ \AA}$ (Pt- S^3) < $2.339 \text{ \AA}$ (Pt- S^2 trans to P). Noticeably, the trans- X^1 -Pt- X^3 bond angles are somewhat bigger than the trans- X^2 -Pt-P bond angles (Table 1).

2.2. 6+5-Membered Metallocyclic Rings

There are five examples that will be discussed in this section, namely $[Pt(\eta^3-C_{16}H_{14}N_2OS_2-O^1,N^1,S^1)(PPh_3)]$ [7], $[Pt(\eta^3-C_{16}H_{13}N_3O_3S_2-O^1,N^1,S^1)(PPh_3)]$ (at 200K) [7], $[Pt(\eta^3-C_8H_8N_3OS-O^1,N^1,S^1)(PPh_3)]$ toluene [8], $[Pt(\eta^3-C_9H_9N_3OS-O^1,N^1,S^1)(PPh_3)]$ (at 100 K) (Figure 2) [9], and $[Pt(\eta^3-C_{18}H_{16}N_2OS_2-O^1,N^1,S^1)(PPh_3)]$ [7] (Table 2). In each of them, the η^3 -ligand creates six- and five-membered metallocyclic rings with a common ligating N^1 atom of the $O^1C_3N^1NCS^1$ type. The values of the respective chelate angles (mean values) are 92.3° (O^1 -Pt- N^1) and 84.6° (N^1 -Pt- S^1). The remaining L-Pt-L bond angles open in the following order (mean values): 90.7° (O^1 -Pt-P) < 92.4° (S^1 -Pt-P) < 175.8° (N^1 -Pt-P) < 175.9° (O^1 -Pt- S^1). Interestingly, the mean values of both trans- O^1 -Pt- S^1 and N^1 -Pt-P angles are equal. The Pt-L bond distance increases (mean values) in the following order: $2.028 \text{ \AA}$ (Pt- O^1 trans to S^1) < $2.035 \text{ \AA}$ (Pt- N^1 trans to P) < $2.244 \text{ \AA}$ (Pt- S^1) < $2.259 \text{ \AA}$ (Pt-P).

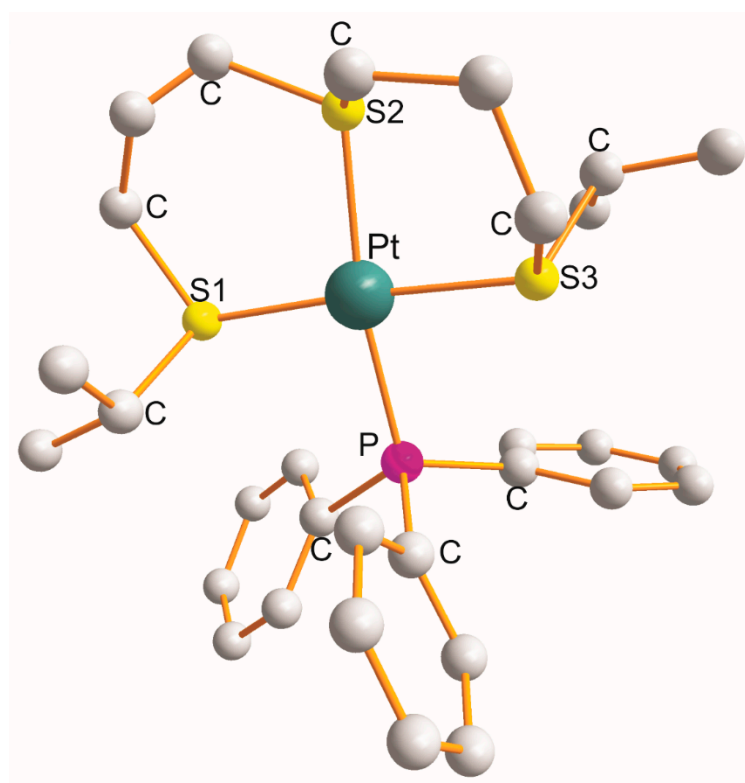


Figure 1. Structure of [Pt(η³-C₁₂H₂₄S₃-S¹,S²,S³)(PPh₃)] [6].

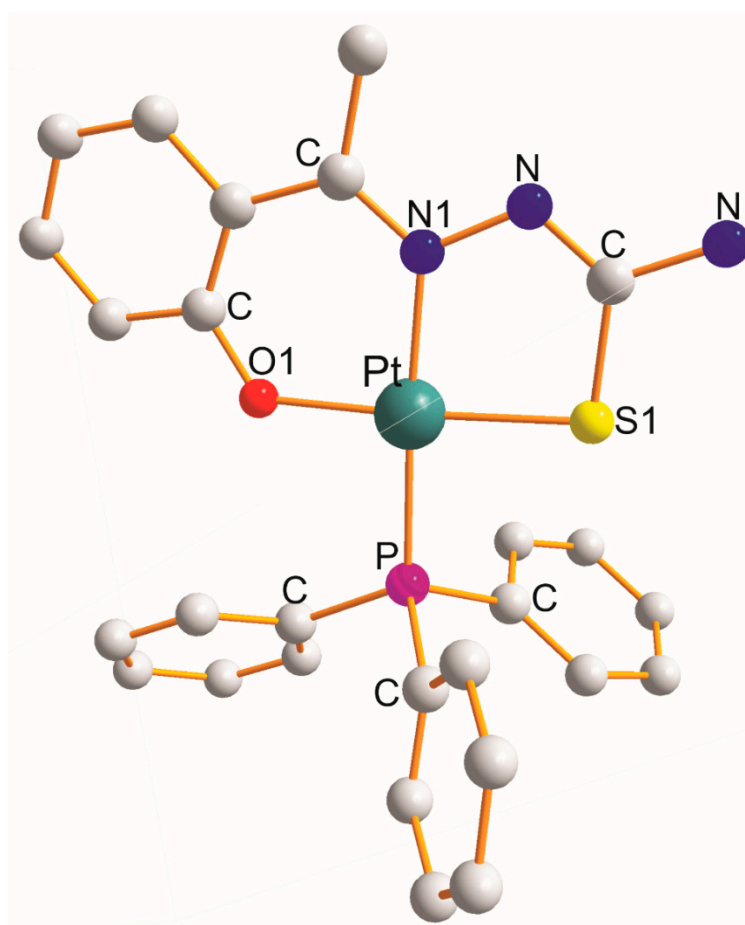


Figure 2. Structure of [Pt(η³-C₉H₉N₃OS-O¹,N¹,S¹)(PPh₃)] [9].

Table 2. Structural data for Pt(η^3 -X₃)(Y) derivatives. ^a—6+5-membered metallocyclic rings.

Complex	Chromophore Chelate Rings τ_4 ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₁₆ H ₁₄ N ₂ OS ₂ -O ¹ ,N ¹ ,S ¹)(PPh ₃)]	PtO ¹ N ¹ S ¹ P (O ¹ C ₃ N ¹ NCS ¹) 0.016	O ¹ 1.992 N ¹ 2.034 S ¹ 2.245 P 2.258	O ¹ ,N ¹ 91.2 ^d N ¹ ,S ¹ 85.0 ^e O ¹ ,S ¹ 176.0 O ¹ ,P 89.0 S ¹ ,P 93.1 N ¹ ,P 178.1 O ¹ ,N ¹ 92.6 ^d N ¹ ,S ¹ 85.3 ^e O ¹ ,S ¹ 177.6 O ¹ ,P 89.0 S ¹ ,P 93.3 N ¹ ,P 176.0 O ¹ ,N ¹ 93.1 ^d N ¹ ,S ¹ 83.8 ^e O ¹ ,S ¹ 176.6 O ¹ ,P 89.9 S ¹ ,P 93.3 N ¹ ,P 176.3 O ¹ ,N ¹ 92.5 ^d N ¹ ,S ¹ 85.1 ^e O ¹ ,S ¹ 175.7 O ¹ ,P 91.5 S ¹ ,P 91.0 N ¹ ,P 175.6 O ¹ ,N ¹ 92.3 ^d N ¹ ,S ¹ 83.2 ^e O ¹ ,S ¹ 173.6 O ¹ ,P 93.1 S ¹ ,P 91.2 N ¹ ,P 173.1	[7]
[Pt(η^3 -C ₁₆ H ₁₃ N ₃ O ₃ S ₂ -O ¹ ,N ¹ ,S ¹)(PPh ₃)] (at 200 K)	PtO ¹ N ¹ S ¹ P (O ¹ C ₃ N ¹ NCS ¹) 0.018	O ¹ 2.001 N ¹ 2.041 S ¹ 2.239 P 2.248		[7]
[Pt(η^3 -C ₈ H ₈ N ₃ OS-O ¹ ,N ¹ ,S ¹)(PPh ₃)]·toluene	PtO ¹ N ¹ S ¹ P (O ¹ C ₃ N ¹ NCS ¹) 0.020	O ¹ 2.015 N ¹ 2.031 S ¹ 2.234 P 2.257		[8]
[Pt(η^3 -C ₉ H ₉ N ₃ OS-O ¹ ,N ¹ ,S ¹)(PPh ₃)] (at 103 K)	PtO ¹ N ¹ S ¹ P (O ¹ C ₃ N ¹ NCS ¹) 0.024	O ¹ 2.085 N ¹ 2.036 S ¹ 2.257 P 2.260		[9]
[Pt(η^3 -C ₁₈ H ₁₆ N ₂ OS ₂ -O ¹ ,N ¹ ,S ¹)(PPh ₃)]	PtO ¹ N ¹ S ¹ P (O ¹ C ₃ N ¹ NCS ¹) 0.037	O ¹ 2.045 N ¹ 2.029 S ¹ 2.246 P 2.269		[7]

(^a) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. (^b) Parameter τ_4 , degree of distortion. (^c) The chemical identity of the coordinated atom/ligand is specific to these columns. (^d) Six-membered metallocyclic ring. (^e) Five-membered metallocyclic ring.

2.3. 5+6-Membered Metallocyclic Rings

There are four complexes mentioned in this section, namely [Pt(η^3 -C₁₂H₁₀N₄-N¹,N²,N³)(PPh₃)] (at 100 K) [10], [Pt(η^3 -C₁₃H₉NO₂-O¹,N¹,O²)(PPh₃)] [11], [Pt(η^3 -C₁₂H₁₆N₂O₄Se₂-Se¹,N¹,Se²)(P(η^1 -C₁₁H₁₉O₅)(Ph)₂)] [12], and [Pt(η^3 -C₂₉H₂₀F₆S₂O-S¹,S²,O¹)(PPh₃)] (at 100 K) [13], and their structural parameters are gathered in Table 3. The structure of [Pt(η^3 -C₁₂H₁₀N₄-N¹,N²,N³)(PPh₃)] [10] is shown in Figure 3 as an example. Each η^3 -ligand creates five and six metallocyclic rings. The donor atoms of the respective η^3 -ligands play a role in the size of the L-Pt-L chelate angles. These angles increase in the following sequences:

N¹C₂N²NC₂N³—81.7° (N¹-Pt-N²) and 89.6° (N²-Pt-N³);
O¹C₂N¹C₃O²—2.4° (O¹-Pt-N¹) and 94.8° (N¹-Pt-O²);
Se¹C₂N¹NC₂Se²—83.3° (Se¹-Pt-N¹) and 98.3° (N¹-Pt-Se²);
S¹C₂S²C₃O¹—90.2° (S¹-Pt-S²) and 99.2° (S²-Pt-O¹).

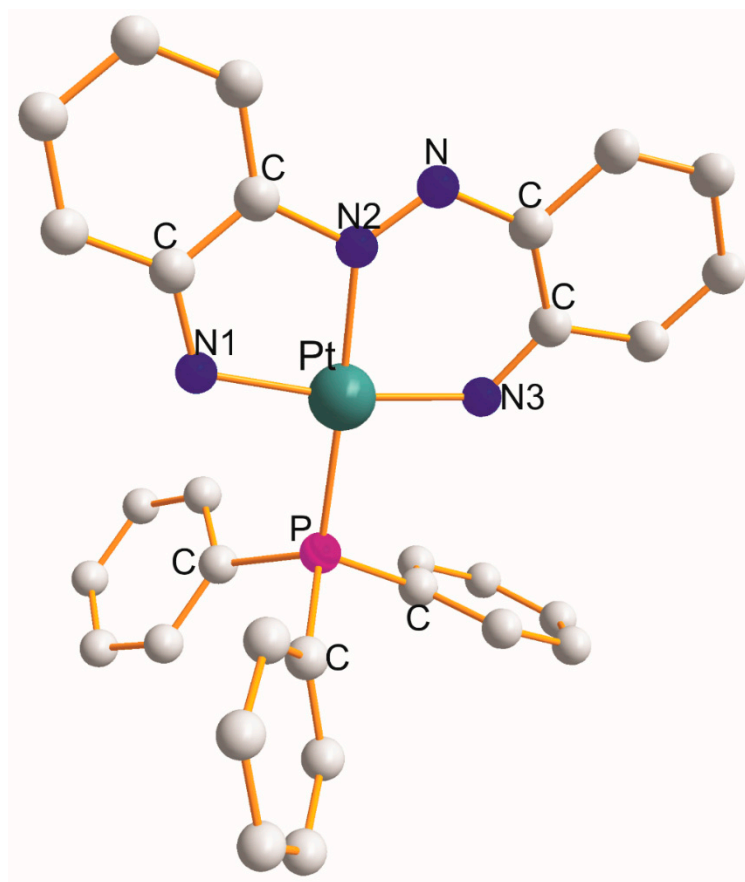


Figure 3. Structure of [Pt(η³-C₁₂H₁₀N₄-N¹,N²,N³)(PPh₃)] [10].

Table 3. Structural data for Pt(η³-X₃)(Y) derivatives. ^a—5+6-membered metallocyclic rings.

Complex	Chromophore Chelate Rings τ ₄ ^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η³-C₁₂H₁₀N₄-N¹,N²,N³)(PPh₃)] (at 100 K)	Pt N¹N²N³P (N¹C₂N²NC₂N³) 0.034	N¹ 1.984 N² 2.025 N³ 1.964 P 2.255	N¹,N² 81.7 ^e N²,N³ 89.6 ^d N¹,N³ 170.6 N¹,P 93.0 N³,P 96.3 N²,P 177.2	[10]
[Pt(η³-C₁₃H₉NO₂-O¹,N¹,O²)(PPh₃)]	Pt O¹N¹O²P (O¹C₂N¹C₃O²) 0.034	O¹ 1.975(9) N¹ 2.064(12) O² 1.996(9) P 2.248	O¹,N¹ 82.4(4) ^e N¹,O² 94.8(4) ^d O¹,O² 176.4(4) O¹,P 91.5(3) O²,P 91.5(3) N¹,P 172.4	[11]
[Pt(η³-C₁₂H₁₆N₂O₄Se²-Se¹,N¹,Se²){P(η¹-C₁₁H₁₉O₅)(Ph)₂}]	Pt Se¹N¹Se² (Se¹C₂N¹NC₂Se²) 0.036	Se¹ 2.394 N¹ 2.078 Se² 2.349 P 2.259	Se¹,N¹ 83.3 ^e N¹,Se² 98.3 ^d Se¹,Se² 176.3 Se¹,P 87.2 Se²,P 90.7 N¹,P 170.9	[12]

Table 3. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 - C ₂₉ H ₂₀ F ₆ O ₄ S ₂ O- S ¹ ,S ² ,O ¹)(PPh ₃)] (at 100 K)	Pt S ¹ S ² O ¹ P (S ¹ C ₂ S ² C ₃ O ¹) 0.059	S ¹ 2.268 S ² 2.277 O ¹ 2.066 P 2.253	S ¹ ,S ² 90.2 ^e S ¹ ,O ¹ 99.2 ^d S ¹ ,O ¹ 169.6 S ¹ ,P 89.2 O ¹ ,P 99.2 S ² P 169.4	[13]

(^a) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. (^b) Parameter τ_4 , degree of distortion. (^c) The chemical identity of the coordinated atom/ligand is specific to these columns. (^d) Six-membered metallocyclic ring. (^e) Five-membered metallocyclic ring.

The monodentate PL displayed distorted square-planar geometry about Pt(II) atoms. The Pt-L bond distance to PL increased in the following order: 2.025 Å (Pt-N²) < 2.064 Å (Pt-N¹) < 2.078 Å (Pt-N¹) < 2.277 Å (Pt-S²). The order follows the above-mentioned sentence for the Pt-L (L is a common central ligating atom between five and six-rings).

2.4. 5+5-Membered Metallocyclic Rings

There are thirty-nine compounds in which each η^3 -ligand creates two five-membered metallocyclic rings. These complexes based on variable combinations of atoms involved in the chelate angles can be divided into twelve groups. Structural data are given in Table 4.

Table 4. Structural data for Pt(η^3 -X₃)(Y) derivatives. ^a—5+5-membered metallocyclic rings.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₃₃ H ₂₄ P ₂ S ₂ - S ¹ ,C ¹ ,S ²)(PPh ₃)]·CH ₂ Cl ₂ (at 193 K)	PtS ¹ C ¹ S ² P (S ¹ PCC ¹ CPS ²) 0.026	S ¹ 2.332 C ¹ 2.020 S ² 2.316 P 2.332	S ¹ ,C ¹ 87.9 ^e C ¹ ,S ² 87.7 ^e S ¹ ,S ² 173.8 S ¹ ,P 89.7 S ² ,P 94.2 C ¹ ,P 176.9	[14]
[Pt(η^3 -C ₁₂ H ₁₀ N ₂ Te ₃ - Te ¹ ,Te ² ,Te ³)(PPh ₃)]·C ₆ H ₆	Pt Te ¹ Te ² Te ³ P (Te ¹ CNTe ² NCTe ³) 0.029	Te ¹ 2.588(3) Te ² 2.569(3) Te ³ 2.612(3) P 2.283(3)	Te ¹ ,Te ² 91.6(2) ^e Te ² ,Te ³ 91.4(2) ^e Te ¹ ,Te ³ 174.0(2) Te ¹ ,P 90.4(2) Te ³ ,P 87.0(2) Te ² ,P 175.5	[15]
[Pt(η^3 -C ₁₀ H ₈ N ₂ Te ₃ - Te ¹ ,Te ² ,Te ³)(PPh ₃)]	Pt Te ¹ Te ² Te ³ P (Te ¹ CNTe ² NCTe ³) 0.044	Te ¹ 2.594 Te ² 2.574 Te ³ 2.572 P 2.282	Te ¹ ,Te ² 92.8(1) ^e Te ² ,Te ³ 92.6(1) ^e Te ¹ ,Te ³ 172.7(2) Te ¹ ,P 86.1(2) Te ³ ,P 89.3(2) Te ² ,P 171.4(2)	[15]

Table 4. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₁₂ H ₉ N ₂ S ₂ B-S ¹ ,B ¹ ,S ²)(PPh ₃)]·0.06CH ₂ Cl ₂ (at 100 K)	PtS ¹ B ¹ S ² P (S ¹ CNB ¹ NCS ²) 0.061	S ¹ 2.304 B ¹ 2.192 S ² 2.275 P 2.384	S ¹ ,B ¹ 79.8 ^e B ¹ ,S ² 85.0 ^e S ¹ ,S ² 161.4 S ¹ ,P 99.8 S ² ,P 95.9 B ¹ ,P 176.7	[16]
[Pt(η^3 -C ₁₃ H ₁₄ N ₅ S ₃ B-S ¹ ,B ¹ ,S ²)(PPh ₃)] (at 100 k)	PtS ¹ B ¹ S ² P (S ¹ CNB ¹ NCS ²) 0.067	S ¹ 2.299 B ¹ 2.192 S ² 2.294 P 2.379	S ¹ ,B ¹ 81.0 ^e B ¹ ,S ² 86.5 ^e S ¹ ,S ² 163.4 S ¹ ,P 98.8 S ² ,P 96.4 B ¹ ,P 172.2	[17]
[Pt(η^3 -C ₂₈ H ₂₄ N ₄ Se ₂ -N ¹ ,N ² ,Se ¹)(PPh ₃)]·0.5H ₂ O	Pt N ¹ N ² Se ¹ P (N ¹ CNN ² NCSe ¹) 0.068	N ¹ 2.020 N ² 1.980 Se ¹ 2.368 P 2.272	N ¹ ,N ² 78.7 ^e N ² ,Se ¹ 82.3 ^e N ¹ ,Se ¹ 162.0 N ¹ ,P 100.0 Se ¹ ,P 98.6 N ² ,P 173.4	[18]
[Pt(η^3 -C ₂₈ H ₂₄ N ₄ S ₂ -N ¹ ,N ² ,S ¹)(PPh ₃)]·0.5thf	PtN ¹ N ² S ¹ P (N ¹ CNN ² NCS ¹) 0.076	N ¹ 2.031 N ² 1.987 S ¹ 2.266 P 2.279	N ¹ ,N ² 78.5 ^e N ² ,S ¹ 81.6 ^e N ¹ ,S ¹ 162.2 N ¹ ,P 99.9 S ¹ ,P 99.7 N ² ,P 172.5	[19]
[Pt(η^3 -C ₁₇ H ₁₂ N ₂ O-O ¹ ,N ¹ ,C ¹)(PPh ₃)]	PtO ¹ N ¹ C ¹ P (O ¹ C ₂ N ¹ NCC ¹) 0.059	O ¹ 2.189 N ¹ 1.997 C ¹ 2.004 P 2.254	O ¹ ,N ¹ 80.9 ^e N ¹ ,C ¹ 79.0 ^e O ¹ ,C ¹ 159.9 O ¹ ,P 99.8 C ¹ ,P 100.1 N ¹ ,P 178.9	[20]
[Pt(η^3 -C ₉ H ₉ N ₃ S-C ¹ ,N ¹ ,S ¹)(PPh ₃)]	PtC ¹ N ¹ S ¹ P (C ¹ C ₂ N ¹ NCS ¹) 0.057	C ¹ 2.045 N ¹ 2.032 S ¹ 2.340 P 2.229	C ¹ ,N ¹ 80.9 ^e N ¹ ,S ¹ 81.7 ^e C ¹ ,S ¹ 162.5 C ¹ ,P 96.6 S ¹ ,P 101.0 N ¹ ,P 176.4	[21]
[Pt(η^3 -C ₁₀ H ₁₁ N ₃ S-C ¹ ,N ¹ ,S ¹)(PPh ₃)]	PtC ¹ N ¹ S ¹ P (C ¹ C ₂ N ¹ NCS ¹) 0.063	C ¹ 2.018 N ¹ 2.029 S ¹ 2.335 P 2.235	C ¹ ,N ¹ 77.9 ^e N ¹ ,S ¹ 83.2 ^e C ¹ ,S ¹ 161.4 C ¹ ,P 98.5 S ¹ ,P 99.9 N ¹ ,P 176.0	[22]
[Pt(η^3 -C ₁₂ H ₁₉ Cl ₂ N ₃ O ₂ S ₃ -C ¹ ,N ¹ ,S ¹)(PPh ₃)]·2NH ₂ SO	PtC ¹ N ¹ S ¹ P (C ¹ C ₂ N ¹ NCS ¹) 0.053	C ¹ 2.038 N ¹ 2.037 S ¹ 2.332 P 2.236	C ¹ ,N ¹ 80.6 ^e N ¹ ,S ¹ 82.8 ^e C ¹ ,S ¹ 163.6 C ¹ ,P 97.0 S ¹ ,P 99.4 N ¹ ,P 177.2	[23]

Table 4. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₉ H ₇ Cl ₂ N ₃ S- C ¹ ,N ¹ ,S ¹)(P(η^3 -C ₆ H ₁₂ N ₃))] (at 173 K)	PtC ¹ N ¹ S ¹ P (C ¹ C ₂ N ¹ NCS ¹) 0.077	C ¹ 2.027 N ¹ 2.035 S ¹ 2.332 P 2.240	C ¹ ,N ¹ 80.7 ^e N ¹ ,S ¹ 83.0 ^e C ¹ ,S ¹ 163.7 C ¹ ,P 98.6 S ¹ ,P 97.6 N ¹ ,P 168.2	[23]
[Pt(η^3 -C ₂₀ H ₃₁ Cl ₂ N ₄ S ₂ - N ¹ ,N ² ,S ¹)(PPh ₃)]·EtOH (at 100 K)	PtN ¹ N ² S ¹ P (N ¹ C ₂ N ² NCS ¹) 0.072	N ¹ 2.042 N ² 2.000 S ¹ 2.270 P 2.268	N ¹ ,N ² 79.0 ^e N ² ,S ¹ 82.0 ^e N ¹ ,S ¹ 161.0 N ¹ ,P 100.0 S ¹ ,P 96.0 N ² ,P 173.0	[24]
[Pt(η^3 -C ₁₈ H ₁₂ N ₂ O- O ¹ ,N ¹ ,C ¹)(PPh ₃)]·MeCN	PtO ¹ N ¹ C ¹ P (O ¹ CNN ¹ C ₂ C ¹) 0.066	O ¹ 2.136 N ¹ 1.995 C ¹ 2.025 P 2.244	O ¹ ,N ¹ 76.0 ^e N ¹ ,C ¹ 81.8 ^e O ¹ ,C ¹ 157.7 O ¹ ,P 103.2 C ¹ ,P 99.1 N ¹ ,P 170.4	[25]
[Pt(η^3 -C ₁₂ H ₂₁ N ₂ - N ¹ ,C ¹ ,N ²)(P(C ₆ H ₄ SO ₃) ₃)] ²⁻ [Pt(η^3 - C ₁₂ H ₂₁ N ₆)(H ₂ O) ₂] (at 150 K)	PtN ¹ C ¹ N ² P (N ¹ C ₂ C ¹ C ₂ N ²) 0.065	N ¹ 2.130 C ¹ 1.971 N ² 2.131 P 2.363	N ¹ C ¹ 80.5 ^e C ¹ ,N ² 79.9 ^e N ¹ ,N ² 159.8 N ¹ ,P 102.6 N ² ,P 97.6 C ¹ ,P 176.8	[26]
[Pt(η^3 -C ₃₀ H ₃₅ N ₅ - N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.067	N ¹ 2.009 N ² 2.022 N ³ 2.010 P 2.243	N ¹ ,N ² 79.1 ^e N ² ,N ³ 78.8 ^e N ¹ ,N ³ 157.5 N ¹ ,P 97.6 N ³ ,P 105.9 N ² ,P 175.7	[27]
[Pt(η^3 -C ₁₁ H ₃ F ₆ N ₇ - N ¹ ,N ² ,N ³)(P(Me)Ph ₂)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.068	N ¹ 2.005 N ² 2.032 N ³ 2.006 P 2.256	N ¹ ,N ² 78.6 ^e N ² ,N ³ 79.2 ^e N ¹ ,N ³ 157.7 N ¹ ,P 100.0 N ³ ,P 102.2 N ² ,P 177.9	[28]
[Pt(η^3 -C ₁₅ H ₁₁ N ₃ - N ¹ ,N ² ,N ³)(P(η^1 - C ₁₄ H ₁₉ O ₅)Ph ₂)]·2SO ₃ CF ₃ · 2Me ₂ CO (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.068	N ¹ 1.998 N ² 2.000 N ³ 2.097 P 2.287	N ¹ ,N ² 79.8 ^e N ² ,N ³ 79.5 ^e N ¹ ,N ³ 158.7 N ¹ ,P 97.9 N ³ ,P 103.0 N ² ,P 176.6	[12]
[Pt(η^3 -C ₁₇ H ₁₁ N-C ¹ ,N ¹ ,C ²) (P(η^1 -C ₁₄ H ₉ O ₅)(Ph) ₂)]·CH ₂ Cl ₂ (at 100 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.086	C ¹ 2.082 N ¹ 2.033 C ² 2.083 P 2.227	C ¹ ,N ¹ 79.4 ^e N ¹ ,C ² 80.1 ^e C ¹ ,C ² 157.3 C ¹ ,P 100.6 C ² ,P 101.0 N ¹ ,P 171.8	[29]

Table 4. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₂₅ H ₁₉ N ₅ -N ¹ ,N ² ,N ³)(PPh ₃)]·3CH ₂ Cl ₂ (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.070	N ¹ 2.015 N ² 2.017 N ³ 1.996 P 2.253	N ¹ ,N ² 79.2 ^e N ² ,N ³ 79.3 ^e N ¹ ,N ³ 158.4 N ¹ ,P 96.9 N ³ ,P 104.6 N ² ,P 176.2	[30]
[Pt(η^3 -C ₂₉ H ₃₃ N ₇ -N ¹ ,N ² ,N ³)(PPh ₃)]·CH ₂ Cl ₂ (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.070	N ¹ 2.012 N ² 2.036 N ³ 2.009 P 2.244	N ¹ ,N ² 78.9 ^e N ² ,N ³ 78.9 ^e N ¹ ,N ³ 157.7 N ¹ ,P 99.9 N ³ ,P 102.2 N ² ,P 177.1	[30]
[Pt(η^3 -C ₁₅ H ₁₁ N ₃ -N ¹ ,N ² ,N ³)(PPh ₃)]·2SO ₃ CF ₃ ^f (at 173 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.070	N ¹ 2.043 N ² 1.978 N ³ 2.052 P 2.276	N ¹ ,N ² 79.6 ^e N ² ,N ³ 80.0 ^e N ¹ ,N ³ 159.2 N ¹ ,P 101.8 N ³ ,P 98.8 N ² ,P 175.4	[31]
	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.082	N ¹ 2.057 N ² 1.975 N ³ 2.040 P 2.288	N ¹ ,N ² 79.9 ^e N ² ,N ³ 79.3 ^e N ¹ ,N ³ 158.5 N ¹ ,P 103.2 N ³ ,P 98.1 N ² ,P 172.0	
[Pt(η^3 -C ₂₂ H ₁₅ N ₇ O-N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.072	N ¹ 2.006 N ² 2.033 N ³ 2.012 P 2.269	N ¹ ,N ² 78.0 ^e N ² ,N ³ 78.3 ^e N ¹ ,N ³ 156.3 N ¹ ,P 101.2 N ³ ,P 102.4 N ² ,P 177.8	[27]
[Pt(η^3 -C ₁₁ H ₃ F ₆ N ₇ -N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.076	N ¹ 2.027 N ² 2.037 N ³ 2.012 P 2.275	N ¹ ,N ² 78.3 ^e N ² ,N ³ 78.5 ^e N ¹ ,N ³ 156.8 N ¹ ,P 97.7 N ³ ,P 105.9 N ² ,P 175.7	[27]
[Pt(η^3 -C ₁₂ H ₆ F ₆ N ₇ O-N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.077	N ¹ 2.015 N ² 2.031 N ³ 2.035 P 2.263	N ¹ ,N ² 78.0 ^e N ² ,N ³ 78.4 ^e N ¹ ,N ³ 156.4 N ¹ ,P 97.6 N ³ ,P 105.9 N ² ,P 175.7	[27]
[Pt(η^3 -C ₁₇ H ₂₁ N ₇ -N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.078	N ¹ 2.022 N ² 2.021 N ³ 2.010 P 2.263	N ¹ ,N ² 78.5 ^e N ² ,N ³ 78.7 ^e N ¹ ,N ³ 157.0 N ¹ ,P 101.0 N ³ ,P 101.9 N ² ,P 174.8	[27]

Table 4. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₁₈ H ₂₃ N ₇ O- N ¹ ,N ² ,N ³)(PPh ₃)] (at 223 K)	PtN ¹ N ² N ³ P (N ¹ C ₂ N ² C ₂ N ³) 0.081	N ¹ 2.016 N ² 2.026 N ³ 2.008 P 2.256	N ¹ ,N ² 78.4 ^e N ² ,N ³ 78.5 ^e N ¹ ,N ³ 156.9 N ¹ ,P 98.4 N ³ ,P 104.6 N ² ,P 173.9	[27]
[Pt(η^3 -C ₁₄ H ₁₀ N ₃ - N ¹ ,N ² ,C ¹)(PPh ₃)]·ClO ₄ (at 173 K)	PtN ¹ N ² C ¹ P (N ¹ C ₂ N ² C ₂ C ¹) 0.065	N ¹ 2.124 N ² 2.022 C ¹ 2.018 P 2.243	N ¹ ,N ² 78.2 ^e N ² ,C ¹ 80.6 ^e N ¹ ,C ¹ 158.8 N ¹ ,P 103.2 C ¹ ,P 97.1 N ² ,P 177.5	[32]
[Pt(η^3 -C ₁₄ H ₁₀ N ₃ - N ¹ ,N ² ,C ¹)(PPh ₃)]·ClO ₄ (at 193 K)	PtN ¹ N ² C ¹ P (N ¹ C ₂ N ² C ₂ C ¹) 0.068	N ¹ 2.101 N ² 2.025 C ¹ 2.005 P 2.227	N ¹ ,N ² 78.5 ^e N ² ,C ¹ 81.1 ^e N ¹ ,C ¹ 159.1 N ¹ ,P 103.0 C ¹ ,P 97.6 N ² ,P 175.8	[32]
[Pt(η^3 -C ₁₄ H ₁₀ N ₃ - N ¹ ,N ² ,C ¹)(PPh ₃)]·ClO ₄ (at 295 K)	PtN ¹ N ² C ¹ P (N ¹ C ₂ N ² C ₂ C ¹) 0.079	N ¹ 2.130 N ² 2.029 C ¹ 2.005 P 2.242	N ¹ ,N ² 79.0 ^e N ² ,C ¹ 81.0 ^e N ¹ ,C ¹ 157.4 N ¹ ,P 101.8 C ¹ ,P 100.6 N ² ,P 174.1	[33]
[Pt(η^3 -C ₂₄ H ₂₀ N ₃ - N ¹ ,N ² ,C ¹)(PPh ₃)]·ClO ₄ (at 113 K)	PtN ¹ N ² C ¹ P (N ¹ C ₂ N ² C ₂ C ¹) 0.072	N ¹ 2.147 N ² 2.022 C ¹ 2.022 P 2.246	N ¹ ,N ² 77.8 ^e N ² ,C ¹ 80.9 ^e N ¹ ,C ¹ 158.2 N ¹ ,P 106.1 C ¹ ,P 97.3 N ² ,P 175.8	[34]
[Pt(η^3 -C ₂₈ H ₂₃ N ₂ - N ¹ ,N ² ,C ¹)(Pcy ₃)]·ClO ₄ · 2MeCN (at 253 K)	PtN ¹ N ² C ¹ P (N ¹ C ₂ N ² C ₂ C ¹) 0.120	N ¹ 2.103 N ² 2.023 C ¹ 2.054 P 2.283	N ¹ ,N ² 78.5 ^e N ² ,C ¹ 79.7 ^e N ¹ ,C ¹ 156.4 N ¹ ,P 101.6 C ¹ ,P 102.4 N ² ,P 160.3	[35]
[Pt(η^3 -C ₁₇ H ₉ F ₂ N-C ¹ ,N ¹ ,C ²) {P(o-tolyl) ₃ }]·CHCl ₃ (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.066	C ¹ 2.085 N ¹ 2.024 C ² 2.094 P 2.255	C ¹ ,N ¹ 79.8 ^e N ¹ ,C ² 79.5 ^e C ¹ ,C ² 158.9 C ¹ ,P 103.1 C ² ,P 97.5 N ¹ ,P 177.3	[36]
[Pt(η^3 -C ₁₈ H ₁₁ F ₂ N-C ¹ ,N ¹ ,C ²) {P(CH ₂ Et) ₃ }] (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.072	C ¹ 2.056 N ¹ 2.027 C ² 2.074 P 2.299	C ¹ ,N ¹ 79.9 ^e N ¹ ,C ² 80.5 ^e C ¹ ,C ² 159.8 C ¹ ,P 102.1 C ² ,P 97.7 N ¹ ,P 174.2	[37]

Table 4. Cont.

Complex	Chromophore Chelate Rings τ_4^b	Pt-L ^c (Å)	L-Pt-L ^c (°)	Ref.
[Pt(η^3 -C ₂₀ H ₁₅ NO ₂ -C ¹ ,N ¹ ,C ²)(PPh ₃)] (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.083	C ¹ 2.075 N ¹ 2.007 C ² 2.073 P 2.252	C ¹ ,N ¹ 79.8 ^e N ¹ ,C ² 80.4 ^e C ¹ ,C ² 159.0 C ¹ ,P 93.2 C ² ,P 103.2 N ¹ ,P 171.0	[38]
[Pt(η^3 -C ₁₈ H ₁₁ F ₂ N-C ¹ ,N ¹ ,C ²){P(CH ₂ Ph) ₃ }]·1.4 CHCl ₃ (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.087	C ¹ 2.062 N ¹ 2.029 C ² 2.071 P 2.241	C ¹ ,N ¹ 79.9 ^e N ¹ ,C ² 80.2 ^e C ¹ ,C ² 158.8 C ¹ ,P 102.2 C ² ,P 98.7 N ¹ ,P 169.8	[39]
[Pt(η^3 -C ₁₇ H ₉ F ₂ N-C ¹ ,N ¹ ,C ²)(PMe ₃)] (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.087	C ¹ 2.070 N ¹ 2.005 C ² 2.065 P 2.243	C ¹ ,N ¹ 79.5 ^e N ¹ ,C ² 80.2 ^e C ¹ ,C ² 158.5 C ¹ ,P 92.0 C ² ,P 102.5 N ¹ ,P 170.0	[40]
[Pt(η^3 -C ₁₇ H ₁₁ N-C ¹ ,N ¹ ,C ²)(PPh ₃)] (at 100 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.087	C ¹ 2.073 N ¹ 2.049 C ² 2.074 P 2.241	C ¹ ,N ¹ 79.7 ^e N ¹ ,C ² 80.2 ^e C ¹ ,C ² 158.8 C ¹ ,P 103.0 C ² ,P 98.7 N ¹ ,P 169.8	[41]
[Pt(η^3 -C ₁₇ H ₉ F ₂ N-C ¹ ,N ¹ ,C ²){P(CH ₂ Ph) ₃ }] (at 150 K)	PtC ¹ N ¹ C ² P (C ¹ C ₂ N ¹ C ₂ C ²) 0.089	C ¹ 2.075 N ¹ 2.033 C ² 2.085 P 2.228	C ¹ ,N ¹ 79.8 ^e N ¹ ,C ² 80.0 ^e C ¹ ,C ² 159.2 C ¹ ,P 103.8 C ² ,P 96.9 N ¹ ,P 168.7	[36]

(^a) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The number in parentheses is the e.s.d. (^b) Parameter τ_4 , degree of distortion. (^c) The chemical identity of the coordinated atom/ligand is specific to these columns. (^e) Five-membered metallocyclic ring. (^f) There are two crystallographically independent molecules.

The structure of [Pt(η^3 -C₃₃H₂₄P₂S₂-S¹,C¹,S²)(PPh₃)]·CH₂Cl₂ [14] is shown in Figure 4. The η^3 -ligand creates two five-membered metallocyclic rings with a common C¹ atom of the S¹PCC¹CPS² type with chelate angles of 87.9° (S¹-Pt-C¹) and 87.7° (C¹-Pt-S²). This is the only example of this type. The PPh₃ demonstrated distorted square-planar geometry about Pt(II) atoms. The remaining L-Pt-L bond angles open in the following order: 89.7° (S¹-Pt-P) < 94.2° (S²-Pt-P) < 173.8° (S¹-Pt-S²) < 176.9° (C¹-Pt-P). The Pt-L bond distance increases in the following order: 2.020 Å (Pt-C¹) < 2.316 Å (Pt-S²) < 2.332 Å (Pt-S¹) < 2.322 Å (Pt-P).

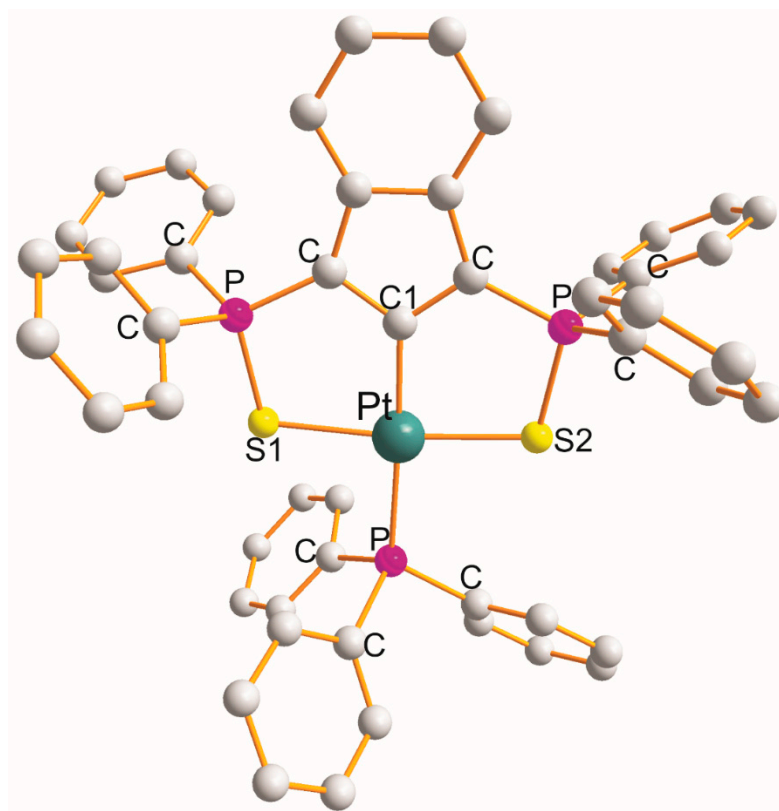


Figure 4. Structure of $[\text{Pt}(\eta^3\text{-C}_{33}\text{H}_{24}\text{P}_2\text{S}_2\text{-S}^1, \text{C}^1, \text{S}^2)(\text{PPh}_3)]$ [14].

In another two complexes, namely $[\text{Pt}(\eta^3\text{-C}_{12}\text{H}_{12}\text{N}_2\text{Te}_3\text{-Te}^1, \text{Te}^2, \text{Te}^3)(\text{PPh}_3)] \cdot \text{C}_6\text{H}_6$ and $[\text{Pt}(\eta^3\text{-C}_{10}\text{H}_8\text{N}_2\text{Te}_3\text{-Te}^1, \text{Te}^2, \text{Te}^3)(\text{PPh}_3)]$ [15], which are isostructural, the η^3 -ligand creates a pair of five-membered metallocyclic rings with common central ligating Te^2 atoms of the $\text{Te}^1\text{CNTe}^2\text{NCTe}^3$ type. The mean values of the respective angles are $92.2 (\pm 6)^\circ$ ($\text{Te}^1\text{-Pt-Te}^2$) and $92.0 (\pm 6)^\circ$ ($\text{Te}^2\text{-Pt-Te}^3$). The PPh_3 ligand demonstrated distorted square-planar geometry about each $\text{Pt}(\text{II})$ atom. The remaining L-Pt-L bond angles open in the following order (mean values): $88.1 (\pm 1.2)^\circ$ ($\text{Te}^3\text{-Pt-P}$) $\sim 88.1 (\pm 2.31)^\circ$ ($\text{Te}^1\text{-Pt-P}$) $< 173.3 (\pm 8)^\circ$ ($\text{Te}^1\text{-Pt-Te}^3$) $< 173.4 (\pm 2.1)^\circ$ ($\text{Te}^2\text{-Pt-P}$). The Pt-L bond distance increases in the following order (mean values): $2.283 (\pm 1) \text{ \AA}$ (Pt-P) $< 2.571 (\pm 2) \text{ \AA}$ (Pt-Te^2) $< 2.591 (\pm 3) \text{ \AA}$ (Pt-Te^1) $< 2.592 (\pm 20) \text{ \AA}$ (Pt-Te^3).

In another two complexes, namely $\text{Pt}(\eta^3\text{-C}_{12}\text{H}_9\text{N}_2\text{S}_2\text{B-S}^1, \text{B}^1, \text{S}^2)(\text{PPh}_3)] \cdot 0.06\text{CH}_2\text{Cl}_2$ [16] and $\text{Pt}(\eta^3\text{-C}_{13}\text{H}_{14}\text{N}_5\text{S}_3\text{B-S}^1, \text{B}^1, \text{S}^2)(\text{PPh}_3)]$ [17], each η^3 -ligand creates a pair of five-membered metallocyclic rings with a common central ligating B^1 atom of the $\text{S}^1\text{CNB}^1\text{NCS}^2$ type. The values of the respective chelate angles are (mean values): $80.4 (\pm 6)^\circ$ ($\text{S}^1\text{-Pt-B}^1$) and $85.7 (\pm 8)^\circ$ ($\text{B}^1\text{-Pt-S}^2$). The PPh_3 demonstrated distorted square-planar geometry about the $\text{Pt}(\text{II})$ atom. The remaining L-Pt-L bond angles open in the following order (mean values): $95.9 (\pm 5)^\circ$ ($\text{S}^2\text{-Pt-P}$) $< 99.3 (\pm 5)^\circ$ ($\text{S}^1\text{-Pt-P}$) $< 162.4 (\pm 1.0)^\circ$ ($\text{S}^1\text{-Pt-S}^2$) $< 174.4 (\pm 2.2)^\circ$ ($\text{B}^1\text{-Pt-P}$). The Pt-L bond distance increases in the following order (mean values): $2.110 (\pm 19) \text{ \AA}$ (Pt-B^1) $< 2.284 (\pm 10) \text{ \AA}$ (Pt-S^2) $< 2.301 (\pm 3) \text{ \AA}$ (Pt-S^1) $< 2.382 (\pm 2) \text{ \AA}$ (Pt-P).

Distorted square-planar geometry about the $\text{Pt}(\text{II})$ atoms in $[\text{Pt}(\eta^3\text{-C}_{28}\text{H}_{24}\text{N}_4\text{Se}_2\text{-N}^1, \text{N}^2, \text{Se}^1)(\text{PPh}_3)] \cdot 0.5\text{H}_2\text{O}$ [18] was achieved by η^3 -ligands with PPh_3 . The η^3 -ligand forms a pair of five-membered metallocyclic rings with a common central ligating N^2 atom of the $\text{N}^1\text{CNN}^2\text{NCS}^1$ type. The values of the respective chelate angles are 78.7° ($\text{N}^1\text{-Pt-N}^2$) and 82.3° ($\text{N}^2\text{-Pt-Se}^1$). The remaining L-Pt-L bond angles increase in the following sequence: 98.6° ($\text{Se}^1\text{-Pt-P}$) $< 100.0^\circ$ ($\text{N}^1\text{-Pt-P}$) $< 162.0^\circ$ ($\text{N}^1\text{-Pt-S}^1$) $< 173.4^\circ$ ($\text{N}^2\text{-Pt-P}$). The Pt-L bond distance increases in the order $1.980 \text{ \AA}$ (Pt-N^2) $< 2.020 \text{ \AA}$ (Pt-N^1) $< 2.272 \text{ \AA}$ (Pt-P) $< 2.368 \text{ \AA}$ (Pt-Se^1).

In $[\text{Pt}(\eta^3\text{-C}_{28}\text{H}_{24}\text{N}_4\text{S}_2\text{-N}^1, \text{N}^2, \text{S}^1)(\text{PPh}_3)] \cdot 0.5\text{thf}$ [19], the η^3 -ligand creates two five-membered metallocyclic rings with common central ligating N^2 atoms of the $\text{N}^1\text{C}_2\text{N}^2\text{NCS}^1$ type with the chelate angles of 78.5° ($\text{N}^1\text{-Pt-N}^2$) and 81.6° ($\text{N}^2\text{-Pt-S}^1$). The PPh_3 demonstrated an inner coordination sphere about the Pt(II) atoms. The remaining L-Pt-L bond angles open in the following order: 99.7° ($\text{S}^1\text{-Pt-P}$) $<$ 99.9° ($\text{N}^1\text{-Pt-P}$) $<$ 162.2° ($\text{N}^1\text{-Pt-S}^1$) $<$ 172.5° ($\text{N}^2\text{-Pt-P}$). The Pt-L bond distance increases in the following sequence: $1.987 \text{ \AA}$ (Pt-N^2) $<$ $2.031 \text{ \AA}$ (Pt-N^1) $<$ $2.266 \text{ \AA}$ (Pt-S^1) $<$ $2.279 \text{ \AA}$ (Pt-P).

Distorted square-planar geometry about the Pt(II) atoms in $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_{12}\text{N}_2\text{O-O}^1, \text{N}^1, \text{C}^1)(\text{PPh}_3)]$ [20] was achieved by η^3 -ligands and PPh_3 . The η^3 -ligand creates two five-membered metallocycles with a common central ligating N^1 atom of the $\text{O}^1\text{C}_2\text{N}^1\text{NCC}^1$ type with the chelate angles of 80.9° ($\text{C}^1\text{-Pt-N}^1$) and 79.0° ($\text{N}^1\text{-Pt-C}^1$). The remaining L-Pt-L bond angles open in the following order: 99.8° ($\text{O}^1\text{-Pt-P}$) $<$ 100.1° ($\text{C}^1\text{-Pt-P}$) $<$ 159.9° ($\text{O}^1\text{-Pt-C}^1$) $<$ 178.9° ($\text{N}^1\text{-Pt-P}$). The Pt-L bond distance increases in the following sequence: $1.997 \text{ \AA}$ (Pt-N^1) $<$ $2.004 \text{ \AA}$ (Pt-C^1) $<$ $2.109 \text{ \AA}$ (Pt-O^1) $<$ $2.254 \text{ \AA}$ (Pt-P).

There are four complexes, namely $[\text{Pt}(\eta^3\text{-C}_9\text{H}_9\text{N}_3\text{S-C}^1, \text{N}^2, \text{S}^1)(\text{PPh}_3)]$ [21], $[\text{Pt}(\eta^3\text{-C}_{10}\text{H}_{11}\text{N}_3\text{S-C}^1, \text{N}^1, \text{S}^1)(\text{PPh}_3)]$ [22], $[\text{Pt}(\eta^3\text{-C}_{12}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}_2\text{S}_3\text{-C}^1, \text{N}^1, \text{S}^1)(\text{PPh}_3)] \cdot 2\text{Me}_2\text{SO}$ [23], and $[\text{Pt}(\eta^3\text{-C}_9\text{H}_7\text{Cl}_2\text{N}_3\text{S-C}^1, \text{N}^1, \text{S}^1)(\eta^3\text{-C}_6\text{H}_{12}\text{N}_3)]$ [23], in which each $\eta^3\text{-C}^1\text{N}^1\text{S}^1$ donor ligand creates two five-membered metallocycles with common central ligating N^1 atoms of the $\text{C}^1\text{C}_2\text{N}^1\text{NCS}^1$ type. The mean values of the chelate angles are $80.1 (\pm 2.2)^\circ$ ($\text{C}^1\text{-Pt-N}^1$) and $82.2 (\pm 1.0)^\circ$ ($\text{N}^1\text{-Pt-S}^1$). The remaining L-Pt-L bond angles open in the following order (mean values): $97.2 (\pm 1.1)^\circ$ ($\text{C}^1\text{-Pt-P}$) $<$ $98.8 (\pm 2.2)^\circ$ ($\text{S}^1\text{-Pt-P}$) $<$ $162.8 (\pm 1.4)^\circ$ ($\text{C}^1\text{-Pt-S}^1$) $<$ $174.5 (\pm 5.9)^\circ$ ($\text{N}^1\text{-Pt-P}$). The Pt-L bond distance increases in the following order (mean values): $2.032 (\pm 14) \text{ \AA}$ (Pt-C^1) $<$ $2.033 (\pm 4) \text{ \AA}$ (Pt-N^1) $<$ $2.229 (\pm 6) \text{ \AA}$ (Pt-P) $<$ $2.332 (\pm 8) \text{ \AA}$ (Pt-S^1).

In $[\text{Pt}(\eta^3\text{-C}_{20}\text{H}_{31}\text{N}_4\text{S}_2\text{-N}^1, \text{N}^2, \text{S}^1)(\text{PPh}_3)] \cdot \text{EtOH}$ [24], the η^3 -ligand forms two five-membered metallocycles with common central ligating N^2 atoms of the $\text{N}^1\text{C}_2\text{N}^2\text{NCS}^1$ type, with the chelate angles of 79.0° ($\text{N}^1\text{-Pt-N}^2$) and 82.0° ($\text{N}^2\text{-Pt-S}^1$). The remaining L-Pt-L angles open in the following order: 96.0° ($\text{S}^1\text{-Pt-P}$) $<$ 100.0° ($\text{N}^1\text{-Pt-P}$) $<$ 161.0° ($\text{N}^1\text{-Pt-S}^1$) $<$ 173.0° ($\text{N}^2\text{-Pt-P}$). The Pt-L bond distance increases in the following order: $2.000 \text{ \AA}$ (Pt-N^2) $<$ $2.042 \text{ \AA}$ (Pt-N^1) $<$ $2.268 \text{ \AA}$ (Pt-P) $<$ $2.270 \text{ \AA}$ (Pt-S^1).

Distorted square-planar geometry in $[\text{Pt}(\eta^3\text{-C}_{18}\text{H}_{12}\text{N}_2\text{O-O}^1, \text{N}^1, \text{C}^1)(\text{PPh}_3)] \cdot \text{MeCN}$ [25] was achieved by η^3 -ligands with PPh_3 . The η^3 -ligand forms two five-membered metallocycles with a common central ligating N^1 atom of the $\text{O}^1\text{C}_2\text{N}^1\text{NCC}^1$ type with the chelate angles of 76.0° ($\text{O}^1\text{-Pt-N}^1$) and 81.8° ($\text{N}^1\text{-Pt-S}^1$). The remaining angles open in the following sequence: 99.1° ($\text{C}^1\text{-Pt-P}$) $<$ 103.2° ($\text{O}^1\text{-Pt-P}$) $<$ 157.7° ($\text{O}^1\text{-Pt-C}^1$) $<$ 176.4° ($\text{N}^1\text{-Pt-P}$). The Pt-L bond distance increases in the following order: $1.995 \text{ \AA}$ (Pt-N^1) $<$ $2.025 \text{ \AA}$ (Pt-C^1) $<$ $2.138 \text{ \AA}$ (Pt-O^1) $<$ $2.244 \text{ \AA}$ (Pt-P).

The structure of $[\text{Pt}(\eta^3\text{-C}_{12}\text{H}_{21}\text{N}_2\text{-N}^1, \text{C}^1, \text{N}^2)\{\text{P}(\text{C}_6\text{H}_4\text{SO}_3)_3\}]^{2-} [\text{Pt}(\eta^3\text{-C}_{12}\text{H}_{21}\text{N}_6)(\text{H}_2\text{O})]_2$ consists of complex anions and complex cations [26]. In a complex anion, a η^3 -ligand via $\text{N}^1, \text{C}^1, \text{N}^2$ atoms with PL ligands achieves distorted square-planar geometry about Pt(II) atoms. This η^3 -ligand creates a pair of five-membered metallocycles with a common central ligating C^1 atom of the $\text{N}^1\text{C}_2\text{C}^1\text{C}_2\text{N}^2$ type. The values of the chelate angles are 80.5° ($\text{N}^1\text{-Pt-C}^1$) and 79.9° ($\text{C}^1\text{-Pt-N}^2$). The remaining L-Pt-L bond angles open in the following sequence: 97.6° ($\text{N}^2\text{-Pt-P}$) $<$ 102.6° ($\text{N}^1\text{-Pt-P}$) $<$ 159.8° ($\text{N}^1\text{-Pt-N}^2$) $<$ 176.8° ($\text{C}^1\text{-Pt-P}$). The Pt-L bond distance increases in the following order: $1.971 \text{ \AA}$ (Pt-C^1) $<$ $2.130 \text{ \AA}$ (Pt-N^1) $<$ $2.131 \text{ \AA}$ (Pt-N^2) $<$ $2.363 \text{ \AA}$ (Pt-P).

In the following eleven complexes, each η^3 -ligand creates a pair of five-membered metallocycles with a common central ligating N^2 atom of the $\text{N}^1\text{C}_2\text{N}^2\text{C}_2\text{N}^3$ type: $[\text{Pt}(\eta^3\text{-C}_{30}\text{H}_{35}\text{N}_5\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ (Sanning et al. 2015) [27], $[\text{Pt}(\eta^3\text{-C}_{11}\text{H}_3\text{F}_6\text{N}_7\text{-N}^1, \text{N}^2, \text{N}^3)\{\text{P}(\text{Me})(\text{Ph}_2)\}]$ [28], $[\text{Pt}(\eta^3\text{-C}_{15}\text{H}_{11}\text{N}_3\text{-N}^1, \text{N}^2, \text{N}^3)\{\text{P}(\eta^1\text{-C}_{14}\text{H}_{19}\text{O}_5)\text{Ph}_2\}] \cdot 2\text{SO}_3\text{CF}_3 \cdot 2\text{MeCO}$ [29], $[\text{Pt}(\eta^3\text{-C}_{25}\text{H}_{19}\text{N}_5\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)] \cdot 3\text{CH}_2\text{Cl}_2$ [30], $[\text{Pt}(\eta^3\text{-C}_{29}\text{H}_{33}\text{N}_7\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)] \cdot \text{CH}_2\text{Cl}_2$ [30], $[\text{Pt}(\eta^3\text{-C}_{15}\text{H}_{11}\text{N}_3\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)] \cdot 2\text{SO}_3\text{CF}_3$ [31], $[\text{Pt}(\eta^3\text{-C}_{22}\text{H}_{15}\text{N}_7\text{O-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ [27], $[\text{Pt}(\eta^3\text{-C}_{11}\text{H}_3\text{F}_6\text{N}_7\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ [27], $[\text{Pt}(\eta^3\text{-C}_{12}\text{H}_6\text{F}_6\text{N}_7\text{O-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ [27], $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_{21}\text{N}_7\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ [27], and $[\text{Pt}(\eta^3\text{-C}_{18}\text{H}_{23}\text{N}_7\text{O-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)]$ [27]. The mon-

odentate PL displayed distorted square-planar geometry about each Pt(II) atom. The total mean values of the chelate angles are $78.9 (\pm 1.0)^\circ$ (N^1 -Pt- N^2) and $79.0 (\pm 1.0)^\circ$ (N^2 -Pt- N^3). The remaining L-Pt-L bond angles open in the following order (total mean values): $99.5 (\pm 3.0)^\circ$ (N^1 -Pt-P) < $102.9 (\pm 2.8)^\circ$ (N^3 -Pt-P) < $157.6 (\pm 1.1)^\circ$ (N^1 -Pt- N^3) < $175.7 (\pm 1.5)^\circ$ (N^2 -Pt-P). The Pt-L bond distance increases in the following order (total mean values): $2.012 (\pm 20) \text{ \AA}$ (Pt- N^1) < $2.012 (\pm 32) \text{ \AA}$ (Pt- N^2) < $2.025 (\pm 32) \text{ \AA}$ (Pt- N^3) < $2.264 (\pm 24) \text{ \AA}$ (Pt-P).

There are five complexes, namely $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]\cdot\text{ClO}_4$ (at 173 K) [32], $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]\cdot\text{ClO}_4$ (at 193 K) [32], $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]\cdot\text{ClO}_4$ (at 245 K) [33], $[\text{Pt}(\eta^3\text{-C}_{24}\text{H}_{20}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]\cdot\text{ClO}_4$ [34], and $[\text{Pt}(\eta^3\text{-C}_{28}\text{H}_{23}\text{N}_2\text{-N}^1, \text{N}^2, \text{C}^1)(\text{Pcy}_3)]\cdot\text{ClO}_4\cdot\text{MeCN}$ [35], in which each η^3 -ligand creates a pair of five-membered metallocycles with a common central ligating N^2 atom of the $N^1\text{C}_2\text{N}^2\text{C}_2\text{C}^1$ type. The structure of $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]$ [32] is shown in Figure 5. The total mean values of the respective chelate angles are $78.4 (\pm 0.6)^\circ$ (N^1 -Pt- N^2) and $80.7 (\pm 1.0)^\circ$ (N^2 -Pt- C^1). The remaining L-Pt-L bond angles open in the following order (total mean values): $99.0 (\pm 3.5)^\circ$ (C^1 -Pt-P) < $103.1 (\pm 2.5)^\circ$ (N^1 -Pt-P) < $158.0 (\pm 1.4)^\circ$ (N^1 -Pt- N^2) < $172.7 (\pm 5.5)^\circ$ (N^2 -Pt-P). The Pt-L bond distance increases in the following order (total mean values): $2.021 (\pm 30) \text{ \AA}$ (Pt- C^1) < $2.030 (\pm 24) \text{ \AA}$ (Pt- N^2) < $2.121 (\pm 18) \text{ \AA}$ (Pt- N^1) < $2.242 (\pm 32) \text{ \AA}$ (Pt-P).

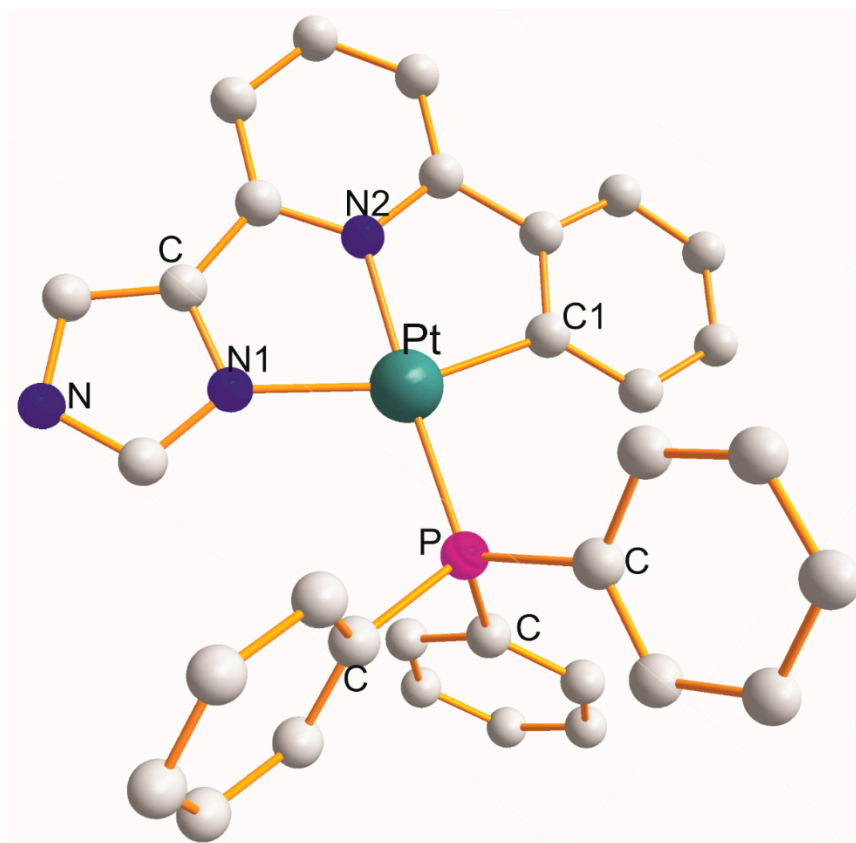


Figure 5. Structure of $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)]$ [32].

In the following eight complexes, each η^3 -ligand creates a pair of five-membered metallocycles with a common central ligating N^1 atom of the $\text{C}^1\text{C}_2\text{N}^1\text{C}_2\text{C}^2$ type: $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_{11}\text{N-C}^1, \text{N}^1, \text{C}^2)\{\text{P}(\eta^1\text{-C}_{14}\text{H}_9\text{O}_5)(\text{Ph})_2\}]\cdot\text{CH}_2\text{Cl}_2$ [29], $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_9\text{F}_2\text{N-C}^1, \text{N}^1, \text{C}^2)\{\text{P}(\eta^1\text{-o-tolyl})_3\}]\cdot\text{CHCl}_3$ (at 150 K) [36], $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_9\text{F}_2\text{N-C}^1, \text{N}^1, \text{C}^2)\{\text{P}(\text{CH}_2\text{Ph})_3\}]\cdot\text{CHCl}_3$ (at 150 K) [36], $[\text{Pt}(\eta^3\text{-C}_{18}\text{H}_{11}\text{F}_2\text{N-C}^1, \text{N}^1, \text{C}^2)\{\text{P}(\text{CH}_2\text{Et})_2\}]\cdot\text{CHCl}_3$ (at 150 K) [37], $[\text{Pt}(\eta^3\text{-C}_{20}\text{H}_{15}\text{NO}_2\text{-C}^1, \text{N}^1, \text{C}^2)(\text{PPh}_3)]$ (at 150 K) [38], $[\text{Pt}(\eta^3\text{-C}_{18}\text{H}_{11}\text{F}_2\text{N-C}^1, \text{N}^1, \text{C}^2)\{\text{P}(\text{CH}_2\text{Ph})_3\}]\cdot\text{CHCl}_3$ (at 150 K) [39], $[\text{Pt}(\eta^3\text{-C}_{12}\text{H}_{11}\text{F}_2\text{N-C}^1, \text{N}^1, \text{C}^2)(\text{PMe}_3)]$ (at 150 K) [40], and $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_{11}\text{N-C}^1, \text{N}^1, \text{C}^2)(\text{PPh}_3)]$ (Figure 6) (at 100 K) [41]. The values of the respective chelate angles are $79.7 (\pm 3)^\circ$ (C^1 -Pt- N^1) and $80.1 (\pm 3)^\circ$ (N^1 -Pt- C^2). The remaining L-Pt-L bond angles open in the following order: $99.5 (\pm 4.2)^\circ$ (C^2 -Pt-P) < $100.0 (\pm 4.5)^\circ$ (C^1 -Pt-P) < $158.5 (\pm 1.4)^\circ$ (C^1 -Pt- C^2) < $171.5 (\pm 4.5)^\circ$ (N^1 -Pt-P). The Pt-L bond distance increases in the

following order (total mean values): $2.026 (\pm 21) \text{ \AA} (\text{Pt-N}^1) < 2.068 (\pm 17) \text{ \AA} (\text{Pt-C}^1) < 2.078 (\pm 6) \text{ \AA} (\text{Pt-C}^2) < 2.249 (\pm 32) \text{ \AA} (\text{Pt-P})$.

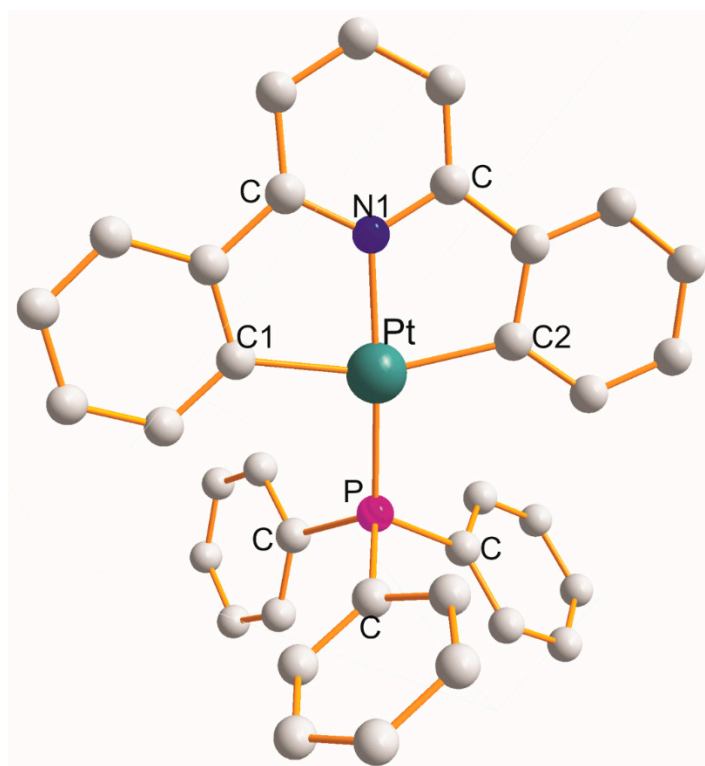


Figure 6. Structure of $[\text{Pt}(\eta^3\text{-C}_{17}\text{H}_{11}\text{N-C}^1, \text{N}^1, \text{C}^2)(\text{PPh}_3)]$ [41].

Each η^3 -ligand creates two five-membered metallocyclic rings. The donor atoms of the respective η^3 -ligands play a role in the size of the L-Pt-L chelate angles. These angles increase in the following sequences:

$\text{N}^1\text{C}_2\text{N}^2\text{C}_2\text{N}^3$: 78.8° ($\text{N}^1\text{C}_2\text{N}^2$), 78.9° ($\text{N}^2\text{C}_2\text{N}^3$) [12,26–28,30,31]

$\text{O}^1\text{CNN}^1\text{C}_2\text{C}^1$: 76.0° (O^1CNN^1), 81.8° ($\text{N}^1\text{C}_2\text{C}^1$) [25]

$\text{N}^1\text{C}_2\text{N}^2\text{C}_2\text{C}^1$: 78.4° ($\text{N}^1\text{C}_2\text{N}^2$), 80.2° ($\text{N}^2\text{C}_2\text{C}^1$) [32–35]

$\text{C}^1\text{C}_2\text{N}^1\text{C}_2\text{C}^2$: 79.7° ($\text{C}^1\text{C}_2\text{N}^1$), 80.2° ($\text{N}^1\text{C}_2\text{C}^2$) [29,36–41]

$\text{N}^1\text{CNN}^2\text{NCS}^1$: 78.5° (N^1CNN^2), 81.6° (N^2NCS^1) [19]

$\text{N}^1\text{C}_2\text{C}^1\text{C}_2\text{N}^2$: 80.5° ($\text{N}^1\text{C}_2\text{C}^1$), 79.9° ($\text{C}^1\text{C}_2\text{N}^2$) [18]

$\text{N}^1\text{CNN}^2\text{NCSe}^1$: 78.7° (N^1CNN^2), 82.3° (N^2NCSe^1) [26]

$\text{O}^1\text{CNN}^1\text{NCC}^1$: 80.9° (O^1CNN^1), 79.0° (N^1NCC^1) [20]

$\text{N}^1\text{C}_2\text{N}^2\text{NCS}^1$: 79.0° ($\text{N}^1\text{C}_2\text{N}^2$), 82.0° (N^2NCS^1) [24]

$\text{C}^1\text{C}_2\text{N}^1\text{NCS}^1$: 77.9° ($\text{C}^1\text{C}_2\text{N}^1$), 83.2° (N^1NCS^1) [21–23]

$\text{S}^1\text{CNB}^1\text{NCS}^2$: 79.8° (S^1CNB^1), 85.0° (B^1NCS^2) [16,17]

$\text{S}^1\text{PCC}^1\text{CPS}^2$: 87.9° (S^1PCC^1), 87.7° (C^1CPS^2) [14]

$\text{Te}^1\text{CNTe}^2\text{NCTe}^3$: 91.6° (Te^1CNTe^2), 91.4° (Te^2NCTe^3) [15]

3. Conclusions

This review includes over fifty monomeric Pt(II) coordination complexes with the composition of $\text{Pt}(\eta^3\text{-X}_3\text{L})(\text{PL})$. There are 14 types of η^3 -ligand coordination via donor atoms ($\text{X}_3 = \text{N}^1\text{N}^2\text{N}^3$; $\text{S}^1\text{S}^2\text{S}^3$; $\text{Te}^1\text{Te}^2\text{Te}^3$; $\text{O}^1\text{N}^1\text{O}^2$; $\text{C}^1\text{N}^1\text{C}^2$; $\text{Se}^1\text{N}^1\text{Se}^2$; $\text{O}^1\text{N}^1\text{C}^1$; $\text{O}^1\text{N}^1\text{S}^1$; $\text{C}^1\text{N}^1\text{S}^1$; $\text{N}^1\text{N}^2\text{C}^1$; $\text{N}^1\text{N}^2\text{S}^1$; $\text{N}^1\text{N}^2\text{Se}^1$; $\text{S}^1\text{O}^1\text{S}^2$; $\text{S}^1\text{B}^1\text{S}^2$; $\text{N}^1\text{O}^1\text{N}^2$; $\text{S}^1\text{S}^2\text{O}^1$) and each η^3 -ligand with monodentate PL displays distorted square-planar geometry about each Pt(II) atom.

Each tridentate ligand creates two metallocyclic rings. Based on the metallocycles, these complexes can be divided into the following four groups with 6+6-; 6+5-; 5+6-; and 5+5-membered metallocyclic rings:

- I. 6+6-membered metallocycles of the $O^1C_3N^1C_3O^2$; $O^1C_2NN^1C_3O^2$ and $S^1C_3S^2C_3S^3$ types with common N^1 and S^2 atoms (three examples) (Table 1);
- II. 6+5-membered metallocycles of the $O^1C_3N^1NCS^1$ type with common central ligating N^1 atoms (five examples) (Table 2);
- III. 5+6-membered metallocycles of the $O^1C_2N^1C_3O^2$; $N^1C_2N^2NC_2N^3$; $Se^1C_2N^1NC_2Se^2$ and $S^1C_2S^2C_3O^1$ types with common central N^1 , ligating N^2 and S^2 atoms (four examples) (Table 3);
- IV. 5+5-membered metallocycles of the $S^1PCC^1CPS^2$; $Te^1CNTe^2NCTe^3$ (2 examples); $S^1CNB^1NCS^2$ (2 examples); $N^1CNN^2NCSe^1$; $N^1CNN^2NCS^1$; $O^1C_2N^1NCC^1$; $C^1C_2N^1NCS^1$ (4 examples); $N^1C_2N^2NCS^1$; $O^1CNN^1C_2C^1$; $N^1C_2C^1C_2N^2$; $N^1C_2N^2C_2N^3$ (11 examples); $N^1C_2N^2C_2C^1$ (5 examples); and $C^1C_2N^1C_2C^2$ (8 examples) types with common central ligating C^1 , Te^2 , B^1 , N^2 and N^1 atoms (39 examples) (Table 4).

The Pt-P (trans to the common central atom) bond distance increases in the following sequence (total mean values): 2.237 Å (N^1) < 2.259 Å (N^2) < 2.283 Å (Te^2) < 2.293 Å (S^2) < 2.348 Å (C^1) < 2.356 Å (B^1), which corresponds quite well with the trans influence of the respective central common donor atoms. The Pt-X (trans to P) bond distance increases in the following sequence (total mean values): 1.995 Å (C^1) < 2.014 Å (N^2) < 2.030 Å (N^1) < 2.109 Å (B^1) < 2.308 Å (S^2) < 2.574 Å (Te^2).

There is a cooperative effect between the covalent radius of the respective donor atoms, the Pt-L bond distance, and chelate rings, as the former grows, the Pt-L bond distance increases and the chelate angles open, as can be observed below (Table 5).

Table 5. Cooperative effects of the respective data.

Chelate rings	L-Pt-L'/L'-Pt-L [°]	Pt-L [Å]
$N^1CNN^2NCS^1$	$78.5^\circ(N^1CNN^2)/81.6^\circ(N^2NCS^1)$ $N = 0.75 \text{ Å}; S = 1.02 \text{ Å}$	1.957(N^2), 2.039(N^1), 2.266(S^1)
$N^1CNN^2NCSe^1$	$78.7^\circ(N^1CNN^2)/82.3^\circ(N^2NCSe^1)$ $N = 0.75 \text{ Å}; Se = 1.16 \text{ Å}$	1.980(N^2), 2.020(N^1), 2.368(Se^1)
$S^1CNB^1NCS^2$	$79.8^\circ(S^1CNB^1)/85.6^\circ(B^1NCS^2)$ $B = 0.82 \text{ Å}; S = 1.02 \text{ Å}$	2.129(B^2), 2.302(S^1), 2.285(S^2)
$Te^1CNTe^2NCTe^3$	$91.6^\circ(Te^1CNTe^2)/91.4^\circ(Te^2NCTe^3)$ $Te = 1.36 \text{ Å}; Te = 1.36 \text{ Å}$	2.572(Te^2), 2.592(Te^1), 2.573(Te^3)

In transition metal complexes, the oxidation state plays a leading role in the geometry formed and platinum is no exception. In four coordinates, Pt(II) prefers square-planar geometry. The utility of a simple metric to assess molecule shape and degree of distortion, as well as to exemplify the τ_4 parameter for square-planar geometry, is demonstrated by the following equations [42]:

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

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141} \text{ For tetrahedral geometry}$$

The values of the τ_4 parameter range from 0.00 for perfect square planar geometry to 1.00 for perfect tetrahedral geometry, since $360 - 2(109.5) = 141$.

The total mean values of trans- α -L-Pt-L (L represents terminal ligating atoms of the respective η^3 -ligand) trans- β -L-Pt-P (L is a common central atom) bond angles, as well as of parameter τ_4 , reflect the membered nature of the respective metallocycles, as can be observed from the data in the following summary (Table 6).

Table 6. Selected data of trans angle and parameter τ_4 of metallocycles.

	Metalloccycles	α -L-Pt-L $^\circ$	β -L-Pt-P $^\circ$	τ_4	Table X
I.	6+6-membered	177.3	174.3	0.023	1
II.	6+5-membered	175.9	174.8	0.026	2
III.	5+6-membered	173.1	172.5	0.040	3
IV.	5+5-membered	162.7	174.9	0.062	4

As can be observed, while the β -L-Pt-P angles are almost constant, the α -L-Pt-L angles are slowly increase with the membered metallocycles in the following sequence: 5+5- < 5+6- < 6+5- < 6+6-. The distortion of the square-planar geometry about Pt(II) atoms decreases in the same sequence, as indicated by parameter τ_4 (0.062 (5+5) > 0.040 (5+6) > 0.024 (6+5) > 0.023 (6+6)).

The coexistence of two or more species that differ only by the degree of distortion of the M-L bond distance and L-M-L bond angles is typical of the general class of distortion isomerism [43]. Over 160 platinum complexes exist following the analysis and classification of isomers [44]. This includes distortion (65%), cis-trans (30%), mixed isomers (cis-trans and distortion), and ligand isomerism.

The complex $[\text{Pt}(\eta^3\text{-C}_{15}\text{H}_{11}\text{N}_3\text{-N}^1, \text{N}^2, \text{N}^3)(\text{PPh}_3)] \cdot 2\text{SO}_3\text{CF}_3$ [31] contains two crystallographically independent molecules within the same crystals (Table 4). These molecules differ by the degree of distortion of Pt-L and L-Pt-L, with the values of parameter τ_4 of 0.070 and 0.082, respectively. Below is a classic example of distortion isomers [43].

As part of the X-ray analysis, $[\text{Pt}(\eta^3\text{-C}_{14}\text{H}_{10}\text{N}_3\text{-N}^1, \text{N}^2, \text{C}^1)(\text{PPh}_3)] \cdot \text{ClO}_4$ was measured at 173 K and 193 K [32], and 295 K [33] (Table 4). It was found that the temperature had an influence on the structural parameters. When the temperature drops, the distortion grows, as indicated by parameter τ_4 in the following order: 0.065 (at 173 K) < 0.068 (at 193 K) < 0.079 (at 295 K). These molecules, as well as independent molecules, are classical distortion isomers [43].

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

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Abbreviations

C ₈ H ₈ N ₃ OS	(salicylaldehyde thiosemicarbazone)
C ₉ H ₉ N ₃ S	(2-(((amino(sulfido)methylene)hydrazono)methyl)-5-methylphenyl)
C ₁₀ H ₈ N ₂ Te ₃	(1,1'-tellanyl)bis(5-pyridine-2-tellurolate)
C ₁₀ H ₁₁ N ₃ S	(4-methylacetophenone thisemicarbazone)
C ₁₁ H ₃ F ₆ N ₇	(2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridinate)
C ₁₁ H ₁₁ N	(2,2'-(pyridine-2,6-diyl)diphenyl)
C ₁₂ H ₂₄ S ₃	(2,12-Diisopropyl-3,7,11-trithiadecane)
C ₁₂ H ₆ F ₆ N ₇ O	(4-methoxy-2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl) pyridinate)
C ₁₂ H ₁₀ N ₂ Te ₃	(1,1'-tellanyl)bis(3-methyl-1λ5-pyridine-2-tellurolate)
C ₁₂ H ₁₁ N ₄	(2-(2-amino)phenyl diazenyl)anilate
C ₁₂ H ₁₆ N ₂ O ₄ Se ₂	diethyl-3,3'-(diazone-1,2-diyl-N)bis(2-(hydroseleno)but-2-enoatato)
C ₁₂ H ₁₉ Cl ₂ N ₃ O ₂ S ₃	(2-(1-((amino(sulfido)methylene)hydrazono)ethyl)-4,5-dichlorophenyl)
C ₁₃ H ₉ NO ₂	N(α,α'-dioxobenzylidene)anilate
C ₁₄ H ₁₀ N ₂ O ₃	(2-(2'-carboxylatophenylazo)-4-methylphenolate)
C ₁₄ H ₁₀ N ₃	(2-(6-(3-1H-pyrazolyl)-2-pyridyl)phenyl)
C ₁₅ H ₁₁ N ₃	(2,2'.6'2''-terpyridine)
C ₁₆ H ₁₃ N ₃ O ₃ S ₂	(4-nitrobenzyl(1-(2-oxidophenyl)ethylidene)carbonodithiohydrazone)
C ₁₆ H ₁₄ N ₂ OS ₂	(benzyl(1-(2-oxidophenyl)ethylidene)carbodithiohydrazone)
C ₁₇ H ₉ F ₂ N	(2,6-(4-fluorophenyl)pyridine)
C ₁₇ H ₁₁ N	(2,2'-(pyridine-2,6-diyl) diphenyl)
C ₁₇ H ₁₂ N ₂ O	(1-(((5-methyl-2-oxodiphenyl)diazinyl)-2-naphtyl)
C ₁₇ H ₂₁ N ₇	(2,6-bis(3-t-butyl-1H-1,2,4-triazol-5-yl))pyridinate)
C ₁₈ H ₁₁ F ₂ N	(5-fluoro-2-{6-(4-fluorobenzene-2-diyl)-3-methylbenzenide)
C ₁₈ H ₁₂ N ₂ O	(1-(((oxidanidyl)(phenyl)methylene)amino)imino)methyl-2-2-naphtyl)
C ₁₈ H ₁₆ N ₂ OS ₂	(benzyl(4-oxido-4-phenylbut-3-en-2-ylidene)carbonodithiohydrazone)
C ₁₈ H ₂₃ N ₇ O	(2,6-bis(3-t-butyl-1H-1,2,4-triazol-5-yl)-4-methoxypyridinate)
C ₂₀ H ₁₅ NO ₂	(2,6-bis(o-phenylene)-4-ethoxycarbonylpyridine)
C ₂₂ H ₁₅ N ₇ O	(4-methoxy-2,6-bis(3-phenyl-1H-1,2,4-triazol-5-yl)pyridinate)
C ₂₄ H ₂₀ N ₃	(2-(4-(4-dimethylaminophenyl)-2,2'-bipyridin-6-yl)phenyl)
C ₂₅ H ₁₉ N ₅	(2,6-bis(3-(4-methyl)-1H-pyrazol-5-yl)pyridinate)
C ₂₈ H ₂₃ N ₂	(3-(4-t-butyl-8-(isoquinolin-3-yl)pyridine-2-yl)-2-naphtyl)
C ₂₈ H ₂₄ N ₄ S ₂	PhSNC(MeC ₆ H ₄)N-NC(MeC ₆ H ₄)NSPh
C ₂₈ H ₂₄ N ₄ Se ₂	PhSeNC(MeC ₆ H ₄)N-NC(MeC ₆ H ₄)NSePh
C ₂₉ H ₃₃ N ₇	(2,6-bis(3-(adamantam-1-yl)-1H-1,2,4-triazol-5-yl)pyridinate)
C ₃₀ H ₃₅ N ₅	(2,6-bis(3-(adamantam-1-yl)-1H-pyrazol-5-yl) pyridinate)
P(C ₁₄ H ₁₉ O ₅)(Ph) ₂	(benzo-15-crown [5] diphenylphosphine
P(CH ₂ Et) ₃	tri-n-propylphosphine
P(CH ₂ Ph) ₃	tribenzylphosphine
P(CH ₃)Ph ₂	methyldiphenylphenylphosphine
PMe ₃	trimethylphosphine
P(tolyl) ₃	tris(2-methylphenyl)phosphine
Pcy ₃	tricyclohexylphosphine
PPh ₃	triphenylphosphine
tfh	tetrahydrofuran

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