Variable Combinations of Tridentate Ligands in Pt(η^3-X_3L)(PL) Derivatives

Subjects: Crystallography

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There are over fifty examples in which the inner coordination spheres about the Pt(II) atoms of the Pt(η^3-X_3L)(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: 1. 6+6-Membered Metallocyclic Rings, 2. 6+5-Membered Metallocyclic Rings, 3. 5+6-Membered Metallocyclic Rings, and 4. 5+5-Membered Metallocyclic Rings.

structure Pt(η3-X3L)(PL) distortion trans-effect

1. 6+6-Membered Metallocyclic Rings

There are only three examples in which a η^3-ligand creates such rings (**Table 1**). In [Pt(η^3-$C_{22}H_{11}F_6N_3O_2$–O^1,N^1,O^2)(PPh_3)] (at 173 K) [1], 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(η^3-$C_{14}H_{10}N_2O_3$–O^1,N^1,O^2)(PPh_3)] (at 150 K) [2]. 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 Å (Pt-O^1 trans to O^2) < 1.996 Å (Pt-O^2) < 2.010 Å (Pt-N^1) < 2.254 Å (Pt-P).

Table 1. Structural data for Pt(η^3-X_3)(Y) derivatives. [a]—6+6-membered metallocyclic rings.

Complex	Chromophore Chelate Rings τ_4 [b]	Pt -L [c] (Å)	L-Pt-L [c] (°)	Ref.
[Pt(η^3-$C_{22}H_{11}F_6N_3O_2$-O^1,N^1,O^2)(PPh_3)] (at 173 K)	$PtO^1N^1O^2P$ ($O^1C_3N^1C_3O^2$) 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	[1]
[Pt(η^3-$C_{14}H_{10}N_2O_3$-O^1,N^1,O^2)(PPh_3)] (at 150 K)	$PtO^1N^1O^2P$ ($O^1C_2NN^1C_3O^2$) 0.024	O^1 1.995(2) N^1 2.000(2)	O^1,N^1 88.2 [d] N^1,O^2 90.0 [d] O^1,O^2 176.5	[2]

Complex	Chromophore Chelate Rings τ_4 [b]	Pt -L [c] (Å)	L-Pt-L [c] (°)	Ref.
		O^2 1.988(2) P 2.251(2)	O^1,P 89.0 O^2,P 90.7 N^1,P 175.0	
[Pt{η^3-$C_{12}H_{24}S_3$-S^1,S^2,S^3}(PPh_3)]BF_4	$PtS^1S^2S^3P$ ($S^1C_3S^2C_3S^3$) 0.035	S^1 2.330(2) S^2 2.339(2) S^3 2.336(2) P 2.332(2)	S^1,S^2 87.1(2) [d] S^2,S^3 89.5(2) [d] 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)	[3]

([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{η^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**) [3]. 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 Å (Pt-S^1) < 2.332 Å (Pt-P) < 2.336 Å (Pt-S^3) < 2.339 Å (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**).

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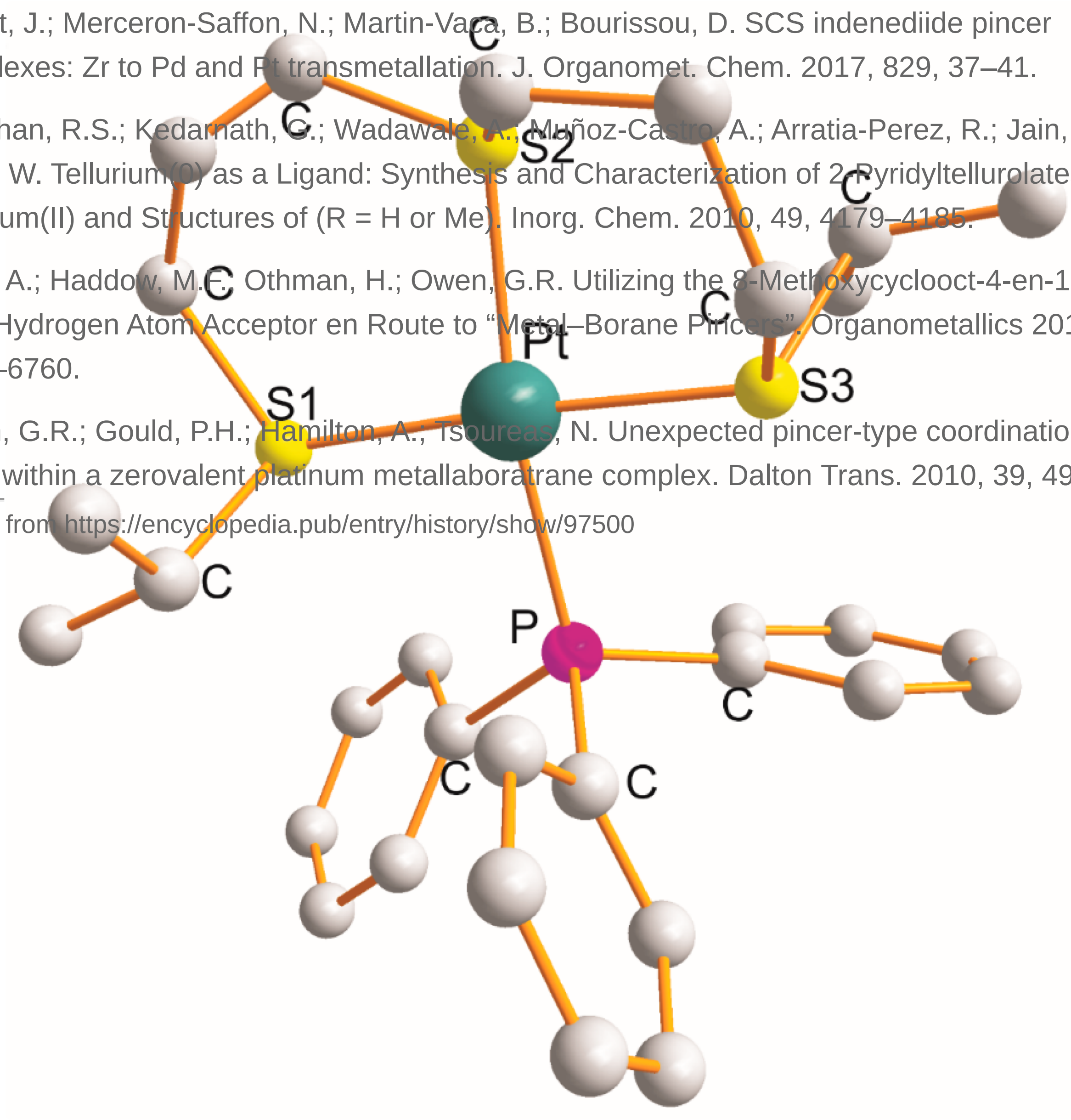

Figure 1. Structure of [Pt{η^3-$C_{12}H_{24}S_3$-S^1,S^2,S^3}(PPh_3)] [3].

2. 6+5-Membered Metallocyclic Rings

There are five examples namely [Pt(η^3-$C_{16}H_{14}N_2OS_2$–O^1,N^1,S^1)(PPh_3)] [4], [Pt(η^3-$C_{16}H_{13}N_3O_3S_2$–O^1,N^1,S^1)(PPh_3)] (at 200K) [4], [Pt(η^3-$C_8H_8N_3OS$–O^1,N^1,S^1)(PPh_3)] toluene [5], [Pt(η^3-$C_9H_9N_3OS$–O^1,N^1,S^1)(PPh_3)] (at 100 K) (**Figure 2**) [6], and [Pt(η^3-$C_{18}H_{16}N_2OS_2$–O^1,N^1,S^1)(PPh_3)] [4] (**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 Å (Pt-O^1 trans to S^1) < 2.035 Å (Pt-N^1 trans to P) < 2.244 Å (Pt-S^1) < 2.259 Å (Pt-P).

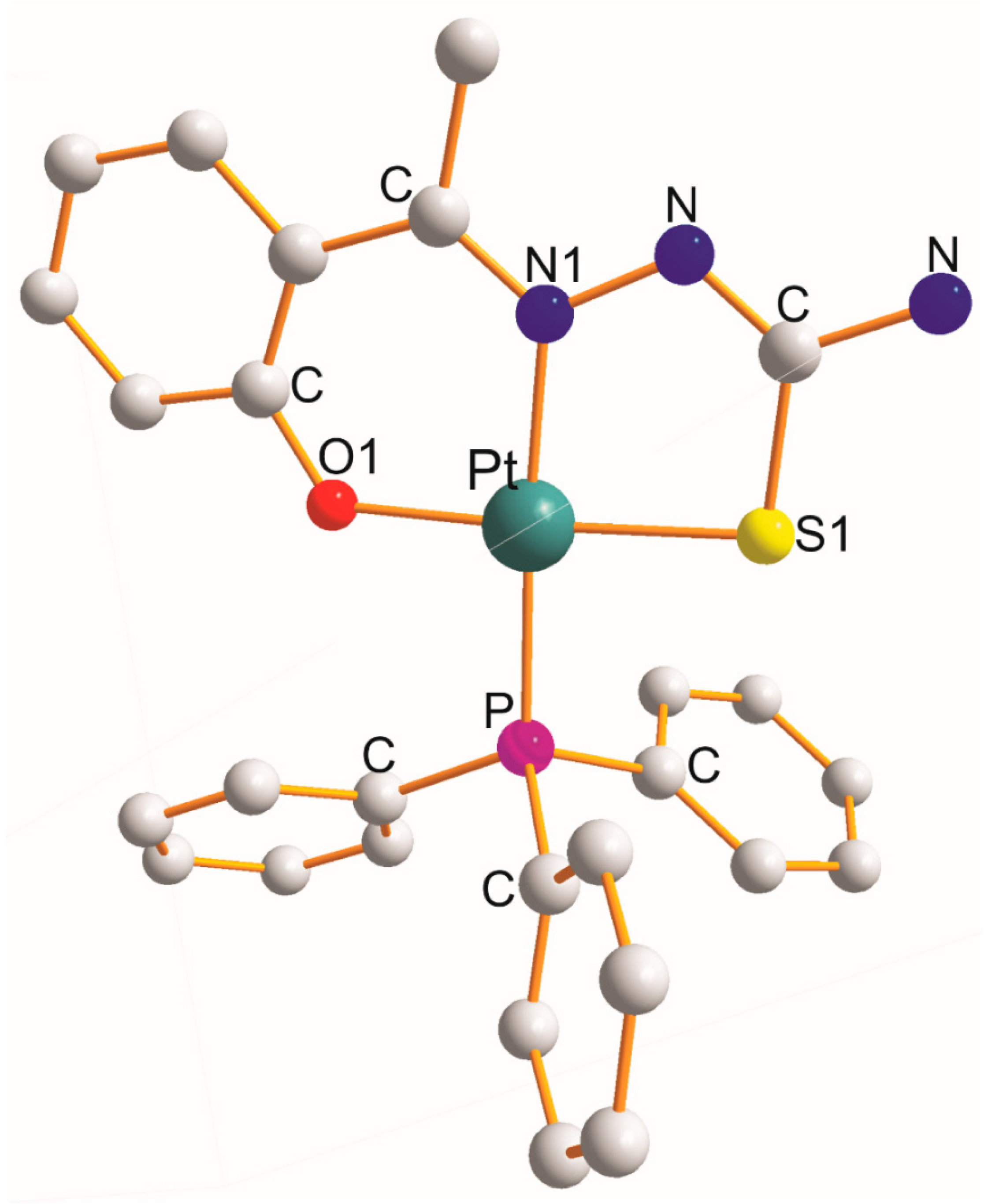

Figure 2. Structure of [Pt(η^3-$C_9H_9N_3OS$–O^1,N^1,S^1)(PPh_3)] [6].

Table 2. Structural data for Pt(η^3-X_3)(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-$C_{16}H_{14}N_2OS_2$-O^1,N^1,S^1)(PPh_3)]	Pt$O^1N^1S^1$P ($O^1C_3N^1NCS^1$) 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	[4]

Complex	Chromophore Chelate Rings τ_4 [b]	Pt -L [c] (Å)	L-Pt-L [c] (°)	Ref.
			S^1,P 93.1 N^1,P 178.1	
[Pt(η^3-$C_{16}H_{13}N_3O_3S_2$-O^1,N^1,S^1)(PPh_3)] (at 200 K)	Pt$O^1N^1S^1$P ($O^1C_3N^1NCS^1$) 0.018	O^1 2.001 N^1 2.041 S^1 2.239 P 2.248	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	[4]
[Pt(η^3-$C_8H_8N_3OS$-O^1,N^1,S^1)(PPh_3)].toluene	Pt$O^1N^1S^1$P ($O^1C_3N^1NCS^1$) 0.020	O^1 2.015 N^1 2.031 S^1 2.234 P 2.257	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	[5]
[Pt(η^3-$C_9H_9N_3OS$-O^1,N^1,S^1)(PPh_3)] (at 103 K)	Pt$O^1N^1S^1$P ($O^1C_3N^1NCS^1$) 0.024	O^1 2.085 N^1 2.036 S^1 2.257 P 2.260	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	[6]
[Pt(η^3-$C_{18}H_{16}N_2OS_2$-O^1,N^1,S^1)(PPh_3)]	Pt$O^1N^1S^1$P ($O^1C_3N^1NCS^1$) 0.037	O^1 2.045 N^1 2.029 S^1 2.246 P 2.269	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	[4]

([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.

3. 5+6-Membered Metallocyclic Rings

There are four complexes mentioned in this section, namely [Pt(η^3-$C_{12}H_{10}N_4$–N^1,N^2,N^3)(PPh_3)] (at 100 K) [7], [Pt(η^3-$C_{13}H_9NO_2$–O^1,N^1,O^2)(PPh_3)] [8], [Pt(η^3-$C_{12}H_{16}N_2O_4Se_2$–Se^1,N^1,Se^2){P(η^1-$C_{11}H_{19}O_5$)($Ph)_2$}] [9], and [Pt(η^3-$C_{29}H_{20}F_6S_2O$–S^1,S^2,O^1)(PPh_3)] (at 100 K) [10], and their structural parameters are gathered in **Table 3**. The structure of [Pt(η^3-$C_{12}H_{10}N_4$–N^1,N^2,N^3)(PPh_3)] [7] 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:

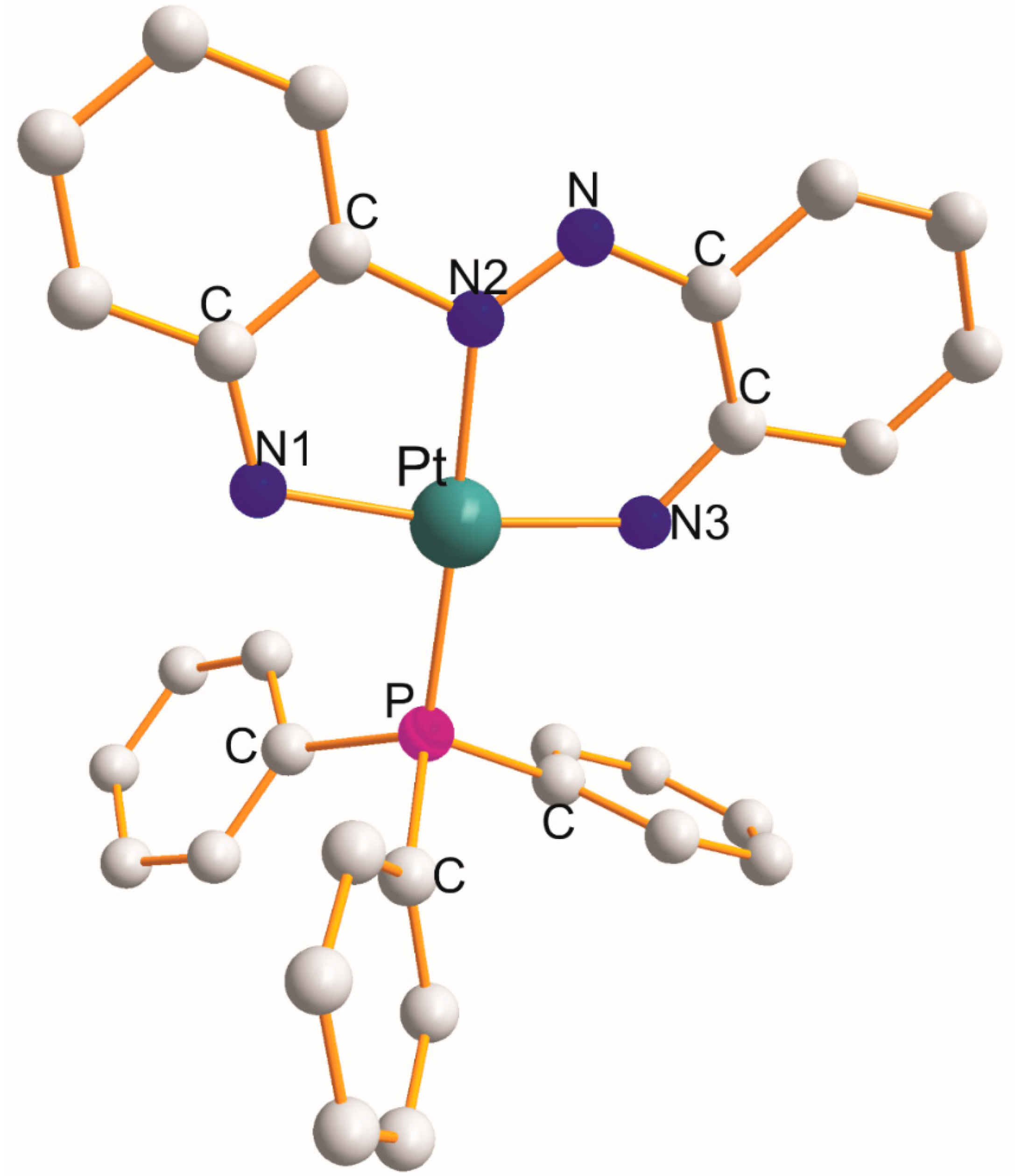

Figure 3. Structure of [Pt(η^3-$C_{12}H_{10}N_4$–N^1,N^2,N^3)(PPh_3)] [7].

Table 3. Structural data for Pt(η^3-X_3)(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(η^3-$C_{12}H_{10}N_4$-N^1,N^2,N^3)(PPh_3)] (at 100 K)	Pt $N^1N^2N^3$P ($N^1C_2N^2NC_2N^3$) 0.034	N^1 1.984 N^2 2.025 N^3 1.964 P 2.255	N^1,N^2 81.7 [e] N^2,N^3 89.6 [d] N^1,N^3 170.6 N^1,P 93.0	[7]

Complex	Chromophore Chelate Rings τ_4 [b]	Pt -L [c] (Å)	L-Pt-L [c] (°)	Ref.
			N^3,P 96.3 N^2,P 177.2	
$[Pt(\eta^3-C_{13}H_9NO_2-O^1,N^1,O^2)(PPh_3)]$	Pt $O^1N^1O^2$P ($O^1C_2N^1C_3O^2$) 0.034	O^1 1.975(9) N^1 2.064(12) O^2 1.996(9) P 2.248	O^1,N^1 82.4(4) [e] N^1,O^2 94.8(4) [d] O^1,O^2 176.4(4) O^1,P 91.5(3) O^2,P 91.5(3) N^1,P 172.4	[8]
$[Pt(\eta^3-C_{12}H_{16}N_2O_4Se_2-Se^1,N^1,Se^2)\{P(\eta^1-C_{11}H_{19}O_5)(Ph)_2\}]$	Pt $Se^1N^1Se^2$ ($Se^1C_2N^1NC_2Se^2$) 0.036	Se^1 2.394 N^1 2.078 Se^2 2.349 P 2.259	Se^1,N^1 83.3 [e] N^1,Se^2 98.3 [d] Se^1,Se^3 176.3 Se^1,P 87.2 Se^2,P 90.7 N^1,P 170.9	[9]
$[Pt(\eta^3-C_{29}H_{20}F_6O_4S_2O-S^1,S^2,O^1)(PPh_3)]$ (at 100 K)	Pt $S^1S^2O^1$P ($S^1C_2S^2C_3O^1$) 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^2P 169.4	[10]

([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.

$N^1C_2N^2NC_2N^3$—81.7° (N^1-Pt-N^2) and 89.6° (N^2-Pt-N^3);

$O^1C_2N^1C_3O^2$—2.4° (O^1-Pt-N^1) and 94.8° (N^1-Pt-O^2);

$Se^1C_2N^1NC_2Se^2$—83.3° (Se^1-Pt-N^1) and 98.3° (N^1-Pt-Se^2);

$S^1C_2S^2C_3O^1$—90.2° (S^1-Pt-S^2) and 99.2° (S^2-Pt-O^1).

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-N^2) < 2.064 Å (Pt-N^1) < 2.078 Å (Pt-N^1) < 2.277 Å (Pt-S^2). The order follows the above-mentioned sentence for the Pt-L (L is a common central ligating atom between five and six-rings).

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.

The structure of [Pt(η^3-$C_{33}H_{24}P_2S_2$–S^1,C^1,S^2)(PPh_3)].CH_2Cl_2 [11] is shown in **Figure 4**. The η^3-ligand creates two five-membered metallocyclic rings with a common C^1 atom of the $S^1PCC^1CPS^2$ type with chelate angles of 87.9° (S^1-Pt-C^1) and 87.7° (C^1-Pt-S^2). This is the only example of this type. The PPh_3 demonstrated distorted square-planar geometry about Pt(II) atoms. The remaining L-Pt-L bond angles open in the following order: 89.7° (S^1-Pt-P) < 94.2° (S^2-Pt-P) < 173.8° (S^1-Pt-S^2) < 176.9° (C^1-Pt-P). The Pt-L bond distance increases in the following order: 2.020 Å (Pt-C^1) < 2.316 Å (Pt-S^2) < 2.332 Å (Pt-S^1) < 2.322 Å (Pt-P).

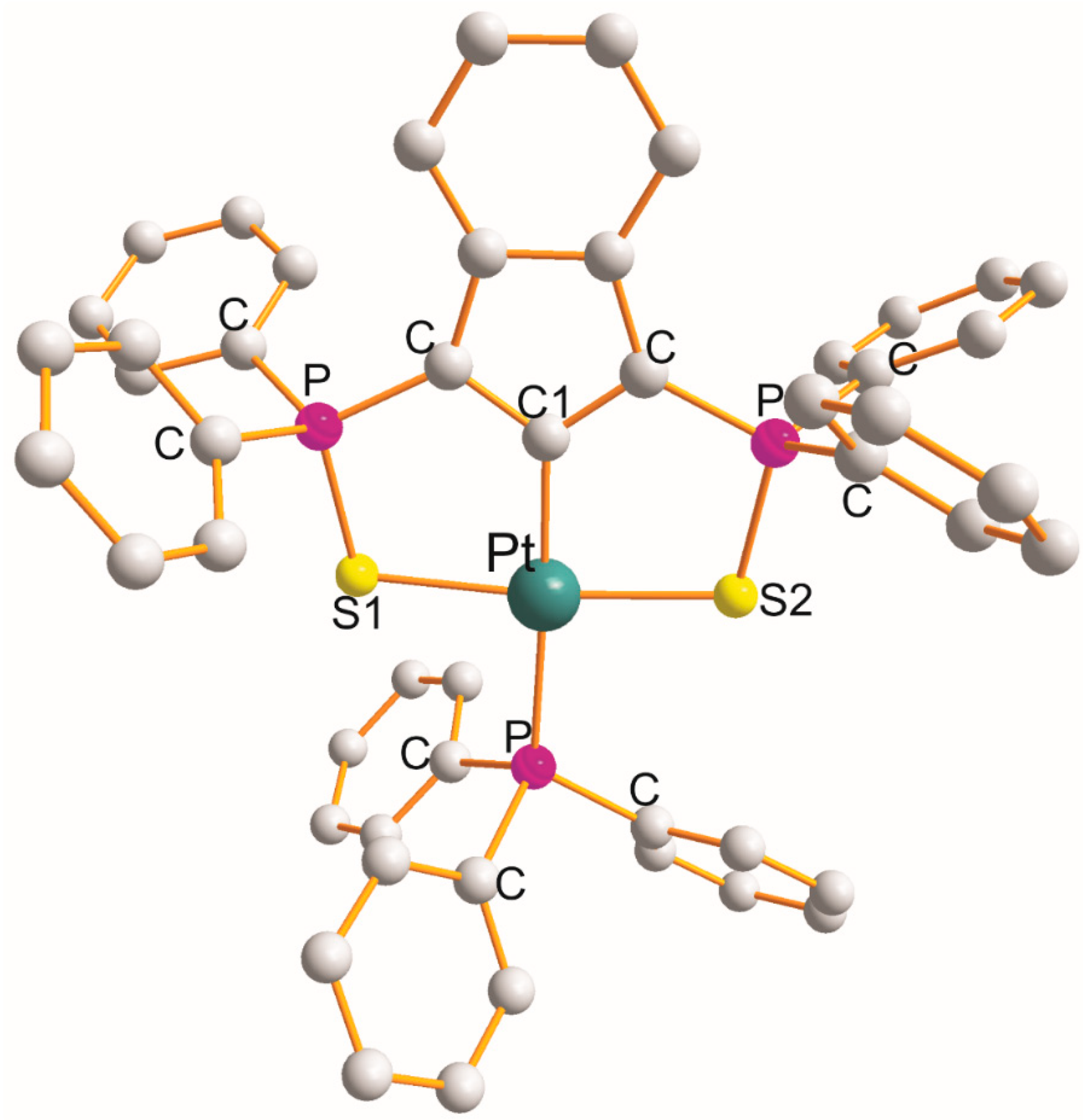

Figure 4. Structure of [Pt(η^3-$C_{33}H_{24}P_2S_2$–S^1,C^1,S^2)(PPh_3)] [11].

In another two complexes, namely [Pt(η^3-$C_{12}H_{12}N_2Te_3$–Te^1,Te^2,Te^3)(PPh_3)].C_6H_6 and [Pt(η^3-$C_{10}H_8N_2Te_3$–Te^1,Te^2,Te^3)(PPh_3)] [12], which are isostructural, the η^3-ligand creates a pair of five-membered metallocyclic rings with common central ligating Te^2 atoms of the $Te^1CNTe^2NCTe^3$ type. The mean values of the respective angles are 92.2 (±6)° (Te^1-Pt-Te^2) and 92.0 (±6)° (Te^2-Pt-Te^3). The PPh_3 ligand demonstrated distorted square-planar geometry about each Pt(II) atom. The remaining L-Pt-L bond angles open in the following order (mean values): 88.1 (±1.2)° (Te^3-Pt-P) ~ 88.1 (±2.31)° (Te^1-Pt-P) < 173.3 (±8)° (Te^1-Pt-Te^3) < 173.4 (±2.1)° (Te^2-Pt-P). The Pt-L bond distance increases in the following order (mean values): 2.283 (±1) Å (Pt-P) < 2.571 (±2) Å (Pt-Te^2) < 2.591 (±3) Å (Pt-Te^1) < 2.592 (±20) Å (Pt-Te^3).

In another two complexes, namely Pt(η^3-$C_{12}H_9N_2S_2B$–S^1,B^1,S^2)(PPh_3)].0.06CH_2Cl_2 [13] and Pt(η^3-$C_{13}H_{14}N_5S_3B$–S^1,B^1,S^2)(PPh_3)] [14], each η^3-ligand creates a pair of five-membered metallocyclic rings with a common central ligating B^1 atom of the $S^1CNB^1NCS^2$ type. The values of the respective chelate angles are (mean values): 80.4

(±6)° (S^1-Pt-B^1) and 85.7 (±8)° (B^1-Pt-S^2). The PPh_3 demonstrated distorted square-planar geometry about the Pt(II) atom. The remaining L-Pt-L bond angles open in the following order (mean values): 95.9 (±5)° (S^2-Pt-P) < 99.3 (±5)° (S^1-Pt-P) < 162.4 (±1.0)° (S^1-Pt-S^2) < 174.4 (±2.2)° (B^1-Pt-P). The Pt-L bond distance increases in the following order (mean values): 2.110 (±19) Å (Pt-B^1) < 2.284 (±10) Å (Pt-S^2) < 2.301 (±3) Å (Pt-S^1) < 2.382 (±2) Å (Pt-P).