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Short Communication

A comprehensive view of metallocycles in Pt(η³–P¹X¹P²)(Y), derivatives-structural aspects

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Abstract

This review covers over one hundred Pt(II) complexes of the compositions Pt(η³–P¹X¹P²)(Y), (X¹ = O¹L, N¹L, C¹L, B¹L, S¹L or Si¹L) and (Y = H, F, Cl, Br, I, O²L, N²L, C²L, or P³L). These complexes crystallized in five crystal classes: monoclinic (60 examples), triclinic (36 examples), orthorhombic (13 examples), trigonal (1 example) and tetragonal (1 example). Each heterotridentate organodiphosphine creates two metallocyclic rings with a common X¹ atom. There are fourteen types of metallocycles from which the $P^1C_2X^1C_2P^2$ is most common. The structural parameters (Pt-L, L-Pt-L) are analyzed and discussed with attention to the distortion of a square-planar geometry about the Pt(II) atoms as well as of trans-influence.

More Information

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Introduction

The high affinity of the Pt(II) ion for phosphorus enables it to bind effectively to organophosphines. Organophosphines as a soft P-donor ligand are very useful for binding a wide variety of platinum complexes. Much attention was paid to organomonophosphines in the chemistry of platinum. There are numerous structural studies of such complexes, which were classified and analyzed [1]. There are also numerous structures of platinum complexes with bidentate organodiphosphines, which were also classified and analyzed [2].

In another the previous reviews we dealt with four-coordinate Pt(η³–P¹X¹P²)(Y), (X¹ = O¹L or N¹L) derivatives [3], Pt(η³–P¹C¹P²)(Y) derivatives (Melník and Mikuš in press) [4] and Pt(η³–P¹X¹P²)(Y), (X¹ = B¹L, S¹L, or Si¹L) derivatives (Melník and Mikuš in press) [5].

The aim of this survey is to correlate the structural parameters for Pt(η³–P¹X¹P²)(Y), (X¹ = O¹L, N¹L, C¹L, B¹L, S¹L, or Si¹L), (Y = H, F, Cl, Br, I, O²L, N²L, C²L, or P³L) derivatives with variable combinations of metallocycles and their influence on the distortion of square-planar geometry, as well as trans-influence of the respective donor atoms.

Results and discussion

There are over one hundred Pt(η³–P¹X¹P²)(Y) derivatives. These complexes are formed by the combination of heterotridentate organodiphosphines and η¹–Y atoms/ligands. Each heterotridentate ligand forms two metallocyclic rings with a common X¹ atom. The complexes can be divided into two main groups, one in which η³–P¹X¹P² ligands create a pair of 'equal' metallocyclic rings and in another one 'dissimilar' ring. There are nine types of 'equal' and five types of 'dissimilar' rings. Selected structural parameters of the complexes from the view of respective metallocyclic rings are given in Table 1A and Table 1B. These complexes crystallized in five crystal classes: monoclinic (60 examples), triclinic (36 examples), orthorhombic (13 examples), trigonal (1 example) and tetragonal (1 example).

Each heterotridentate organodiphosphine ligand creates two-metallocyclic rings with a common X¹ atom. There are at least two contributing factors to the size of the L-Pt-L chelate bond angles both ligand-based. One is the steric constraints imposed by the ligand and the other is the need to accommodate the imposed ring size. The effect of both steric and electronic factors can be seen from the values of the L-Pt-L chelate angles. These angles open in the sequences (mean values):

A. Table 1A

Table 1A	
Pt(η³–P¹C_2X¹C_2P²)(Y):	X¹ = O¹, 81.6 (±9)°, Y = P³ph_3; 1 example;
(5 + 5 metallocycles)	X¹ = C¹, 82.7 (±2.8)°, Y = NI, OI, Br, Cl, C²; 31 examples;
	X¹ = N¹, 83.2 (±1.9)°, Y = Cl, N²I, P²I, CL; 19 examples;
	X¹ = Si¹, 83.9 (±4.1)°, Y = OL, Cl, NL, H, CL; 13 examples;
Pt(η³–P¹OCX¹COP²)(Y):	X¹ = C¹, 80.6 (±8)°, Y = F, Cl, I; 10 examples;
(5 + 5 metallocycles)	X¹ = N¹, 82.0 (±4)°, Y = Cl, CL; 3 examples;
Pt(η³–P¹NCX¹CNP²)(Y):	X¹ = N¹, 81.1 (±1)°, Y = Cl; 1 example;
(5 + 5 metallocycles)	X¹ = C¹, 82.2 (±4)°, Y = Br; 1 example;
Pt(η³–P¹CNX¹NCP²)(Y):	X¹ = B¹, 79.1 (±4)°, Y = OI, Cl, H; 4 examples;
(5 + 5 metallocycles)	X¹ = Si¹, 84.8 (±1.1)°, Y = Cl; 1 example;
Pt(η³–P¹CPX¹PCP²)(Y):	X¹ = C¹, 88.5 (±1.9)°, Y = Cl; 2 examples;
(5 + 5 metallocycles)	
Pt(η³–P¹C_3X¹C_3P²)(Y):	X¹ = C¹, 87.4 (±1.0)°, Y = Br; 1 example;
(6 + 6 metallocycles)	X¹ = Si¹, 89.8 (±6)°, Y = Cl; 1 example;
Pt(η³–P¹NC_2X¹C_2NP²)(Y):	X¹ = N¹, 83.9 (±1.0)°, Y = H; 1 example;
(6 + 6 metallocycles)	X¹ = C¹, 84.6 (±6)°, Y = Cl; 1 example;
Pt(η³–P¹C_2NX¹NC_2P²)(Y):	X¹ = C¹, 87.7 (±1.7)°, Y = H, Cl; 2 examples;
(6 + 6 metallocycles)	
Pt(η³–P¹C_4X¹C_4P²)(Y):	X¹ = O¹, 88.5 (±1.5)°, Y = CH_3; 1 example;
(7 + 7 metallocycles)	

B. Table 1B

Table 1B	
Pt(η³–P¹C_2X¹NCP²)(Y):	X¹ = C¹, 82.2/79.0°, Y = Cl; 1 example;
(5 + 5' metallocycles)	
Pt(η³–P¹C_2X¹C_3P²)(Y):	X¹ = n¹, 80.8/95.1°, Y = Cl; 1 example;
(5 + 6 metallocycles)	X¹ = C¹, 84.2/86.6°, Y = C²L; 1 example;
Pt(η³–P¹C_2X¹NC_2P²)(Y):	X¹ = N¹, 80.7/91.2°, Y = Cl; 1 example;
(5 + 6 metallocycles)	
Pt(η³–P¹C_2X¹CNC_2P²)(Y):	X¹ = N¹, 82.8/96.3°, Y = C²L; 1 example;
(5 + 7 metallocycles)	
Pt(η³–P¹C_2X¹$(C_2O)_3C_2$P²)(Y):	X¹ = O¹, 81.3/175.9°, Y = O²L; 1 example.
(5 + 14 metallocycles)	

The total mean values of the Pt-X¹ bond distance elongates in the sequence:

Pt-O¹ (trans to Y): 2.152Å (C²L) < 2.162Å (O²L) < 2.189Å (P³L);

Pt-N¹ (trans to Y): 2.023(±23)Å (Cl) < 2.024Å (N²L) < 2.077(±5)Å (P³L) < 2.122(±16)Å (C²L) < 2.152Å (H);

Pt-C¹ (trans to Y): 1.964Å (F) < 2.000(±12)Å (I) < 2.001(±8)Å (N²L) ~ 2.001(±85)Å (Cl) < 2.026(±20)Å (Br) < 2.027(±8)Å (O²L) < 2.049(±4)Å (H) < 2.062(±15)Å (C²L);

Pt-B¹ (trans to Y): 1.965(±9)Å (O²L) < 1.981Å (Cl) < 2.012Å (H);

Pt-S¹ (trans to Y): 2.187(±5)Å (Cl) < 2.256Å (I) < 2.268Å (C²L) < 2.328(±15)Å (P³L);

Pt-Si¹ (trans to Y): 2.275(±5)Å (O²L) < 2.282(±20)Å (Cl) < 2.315Å (N²L) < 2.331(±5)Å (H) < 2.339(±14)Å (C²L).

The total mean values of the Pt-Y (trans to X¹) bond distance elongates in the sequence:

Pt-Y (trans to O¹): 2.066Å (C²L) < 2.111Å (O²L) < 2.239Å (P³L);

Pt-Y (trans to N¹): 1.690Å (H) < 2.000(±35)Å (C²L) < 2.052Å (N²L) < 2.240(±60)Å (Cl) < 2.277Å (P³L);

Pt-Y (trans to C¹): 1.530Å (H) < 2.004(±65)Å (C²L) < 2.060Å (F) < 2.085(±12)Å (N²L) < 2.132(±5)Å (O²L) < 2.370(±5)Å (Cl) < 2.475(±15)Å (Br) < 2.482(±6)Å (I);

Pt-Y (trans to B¹): 2.070 Å (H) < 2.294(±11) Å (O²L) < 2.453 Å (Cl);

Pt-Y (trans to S¹): 2.093Å (C²L) < 2.285(±4)Å (P³L) < 2.317(±1)Å (Cl) < 2.510Å (I);

Pt-Y (trans to Si¹): 1.510Å (H) < 2.122(±6)Å (C²L) < 2.222Å (N²L) < 2.282Å (O²L) < 2.306(±10)Å (Cl).

The total mean values of the Pt-P (mutually trans) bond distance elongates in the sequence of X¹:

Pt-P (mutually trans) (X¹): 2.278(±40)Å (C¹) < 2.283(±35)Å (N¹) < 2.292(±40)Å (Si¹) < 2.293 (±30)Å (O¹) < 2.298(±19)Å (S¹) < 2.311(±30)Å (B¹).

It is well known that in four coordinate Pt(II) prefer a square planar geometry. The utility of a simple metric to assess molecule shape and degree of distortion as well as exemplified best the τ_4 parameter for a square planar geometry by the equation introduced by [6];

$\tau_4 = 360 - (\alpha + \beta)/360$, for square planar and

$\tau_4 = 360 - (\alpha + \beta)/141$ for tetrahedral.

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

The total mean values of τ_4 for the respective complexes growing in the sequences:

Pt(η³–P¹O¹P²)(Y): 0.037 (Y = C²L) < 0.039 (O²L) < 0.064 (P³L);

Pt(η³–P¹N¹P²)(Y): 0.035 (Y = H) < 0.046 (Cl) < 0.049 (N²L) < 0.054 (C²L) < 0.075 (P³L);

Pt(η³–P¹C¹P²)(Y): 0.025 (Y = H) < 0.045 (Br) < 0.048 (C²L) < 0.050 (Cl) < 0.054 (I) < 0.056 (F) < 0.057 (O²L) < 0.064 (N²L);

Pt(η³–P¹S¹P²)(Y): 0.041 (C²L) < 0.047 (I) < 0.054 (Cl) < 0.056 (P³L);

Pt(η³–P¹Si¹P²)(Y): 0.048 (Y = O²L) < 0.056 (Cl) < 0.064 (C²L) < 0.066 (H);

Pt(η³–P¹B¹P²)(Y):0.073 (Y = H) ~ 0.073 (Cl) < 0.078 (O²L)

The distortion of the square-planar geometry increases in the given sequences. There is a cooperative effect between a degree of distortion and trans influence of Y atom/ligand when trans influence of the respective Y weakness degree of distortion increases.

We believe that such a review as this can continue to serve a useful function by centralizing available material and delineating areas worthy of further investigation.

Note: For References of the respective complexes are given in our previous reviews Pt(η³−P¹X¹P²)(Y), X¹ = O¹L, or N¹L) (Melník and Mikuš 2021) [3]; Pt(η³−P¹C¹P²)(Y), (Melník and Mikuš, in press) [4] and Pt(η³−P¹X¹P²)(Y), (X¹ = B¹L, S¹L or Si¹L) (Melník and Mikuš in press) [5], therefore are not repeat in this summarise paper.

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