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Review

Organophosphines in organoplatinum complexes structural aspects of $PtPC_3$ and PtP_2CX ($X = H$, F or OL) derivatives

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ABSTRACT

In this review are summarized and analyzed structural parameters of over one hundred monomeric complexes with $PtPC_3$ and PtP_2CX ($X = H$, F or OL) chromophores. These complexes crystallized in four crystal systems: trigonal (×1), orthorhombic (×14) triclinic (×22) and monoclinic (×70). The inner coordination sphere ($PtPC_3$) is build up by monodentate (PL,CL), homobidentate- (C,C), heterobidentate- (C,P) and even homotridentate- (C,C,C) donor sites ligands. The PtP_2CH is build up by monodentate (PL, CL and H atom), homobidentate- (P,P), heterobidentate- (C,P) and even (H,P) donor sites ligands. The PtP_2CF by monodentate (PL, CL and F atom) and homobidentate- (P,P) donor sites ligands. The PtP_2CO, by monodentate (PL, CL and OL), homobidentate- (P,P), heterobidentate- (P,C; P,O; and O,C) and hetero-tridentate- (P,C,P) donor sites ligands. The chelating ligands form wide variety of metallocycles with three-, four-, five-, six- and even seven-membered rings. There are two types of isomers cis-, trans- and distortion, the latter prevails. Several relationships were found and discussed. Noticeable, while PtP_2CH complexes with cis-configuration are somewhat less crowded but higher distorted than those with trans-configuration, in the complexes with PtP_2CX ($X = F$ or O) inner coordination spheres opposite is true.

Contents

1. Introduction 1
2. $PtPC_3$ derivatives 2
3. PtP_2CX ($X = H$, F or OL) DERIVATIVES 2
    3.1. PtP_2CH derivatives 2
    3.2. PtP_2CF derivatives 3
    3.3. PtP_2CO derivatives 3
4. Conclusions 5
Acknowledgements 6
Abbreviations 6
References 6

1. Introduction

Platinum atom has played important role in the development of organometallic chemistry. Considerable research activity has been invested in platinum complexes their synthesis and properties. This has included a considerable number of structural determinations which have helped to shed light on catalytically and other activity.

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Organophosphines as a soft donor ligands are very attractive in the chemistry of organoplatinum complexes. We turn over attention on such complexes. Recently, we classified and analyzed structural parameters of a few hundred monomeric platinum complexes with an inner coordination sphere of PtP_3C and *trans*-PtP_2C_2 [1] and *cis*-PtP_2C_2 [2]. In this review the compounds of composition $PtPC_3$ and PtP_2CX (X = H, F or OL) are surveyed.

The primary source of information has been the Cambridge Crystallographic Data base up to the end of 2015. Derivatives have been classified on the basis of increasing covalent radius of X atom. Within each chromophore, ordering is based on increasing size of the metallocyclic ring. As previously, some cases present insufficient data to atomic coordinates can confuse the interpretation of the actual chromophore present, and sometimes the identity of the actual ligand is useless.

The aim of this survey is to correlate the structural information available, and try to identify factors which may be responsible for the observed stereochemistry of the over one hundred organoplatinum complexes included in this review.

2. $PtPC_3$ derivatives

There are fourteen such complexes which crystallized in two crystal systems orthorhombic (×3) and monoclinic (×11). In seven of them: $(NBu_4)[Pt(PPh_3)(C_6F_5)_3]$ [3], $(NMe_4)[Pt(PPh_3)(CF_3)_3]$ [4], $(NBu_4)[Pt\{P(o\text{-tolyl})_3\}(CF_3)_3]$ [5], $[Pt(MePPh_3)_2(C_5H_4O).(PPh_3)](BF_4)_2$ [6], *cis*-$[Pt(PPh_3)(C_6F_5)_2\{\eta^1\text{-}C_{24}H_{21}O_4P\}]CH_2Cl_2$ [7], orthorhombic *cis*-, and monoclinic *trans*-$[Pt(PPh_3)(\eta^1\text{-}C_9H_9N_2O_7)_2(CO)]$ [8], only monodentate donor ligands created $PtPC_3$ inner coordination sphere. The mean Pt-C bond distances are 2.04 Å (trans to C) and 2.06 Å (trans to P) and the mean Pt-P bond distance is 2.28 Å. The mean C-Pt-C bond angles are 87.0° and 173.5°, and C-Pt-P are 93.0° and 176.7°.

In two *cis*-$[Pt(PBu^t_3)(\eta^2\text{-}C{\equiv}CPh)(CO)]$ [9], and $[Pt(PBu^t_3)(\eta^2\text{-}F_3CC{\equiv}CCF_3)(CO)]$ [10], each chelating-C,C donor ligand forms three-membered metallocyclic ring with the mean C-Pt-C bite angle of 38° (C≡C). In another two *cis*-$[Pt(\eta^2\text{-}C_{20}H_{31}N_2P)(Me)_2]$ (Fig. 1) [11] and $[Pt(\eta^2\text{-}C_{23}H_{37}N_2P)(Me)_2]$ [11], each chelating-C,P donor ligand forms four-membered metallocyclic ring with the mean C-Pt-P bite angle of 69° (CNP).

In another two complexes: $[Pt\{\eta^2\text{-}C_{21}H_{20}P\}(C{\equiv}CPh)(CO)]Me_2CO$ [12] and *cis*-$(NBu^t)[Pt\{\eta^2\text{-}C_{21}H_{20}P\}(C{\equiv}CPh)_2]$ [12] the chelating ligand forms five-membered metallocyclic ring with the mean C-Pt-P bite angle of 82.5 (CC_2P).

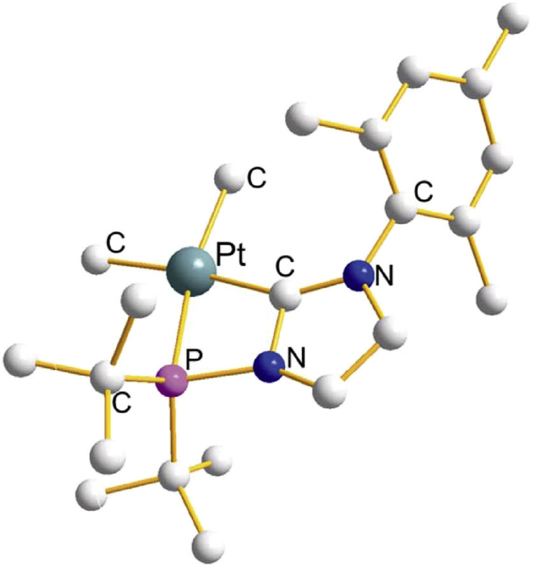

Fig. 1. Structure of *cis*-$[Pt(\eta^2\text{-}C_{20}H_{31}N_2P)(Me)_2]$ [11].

In monoclinic *cis*-$[Pt(PPh_3)(\eta^2\text{-}C_{21}H_{21}O_4S)(Bu^tNC)]CHCl_3$ [13] the chelating ligand forms five-membered metallocycle with the value of C-Pt-C bite angle of 82.3° (CCSC). Remaining *cis*-L-Pt-L bond angles are 94.5° (C-Pt-C) and 91.5° (C-Pt-P). The Pt-L bond distances are 1.91 Å (CO), 2.02 Å (C, trans to C), 2.07 Å (C, trans to P) and 2.325 Å (P).

In monoclinic $[Pt(PPh_3)\{\eta^3\text{-}CH_2C(Me)CH_2\}]PF_6$ [14] homo-terdentate-C,C,C ligand with PPh_3 ligand created a distorted square-planar geometry about Pt(II) atom. Unfortunately only Pt-C bond distances with the mean values of 2.20 and 2.23 Å were given in the original paper.

3. PtP_2CX (X = H, F or OL) DERIVATIVES

There are almost one hundred such derivatives for which structural parameters are available. The structural parameters are classified and analyzed especially from the coordination mode of the respective donor ligands. There are complexes with cis-as well trans-configurations.

3.1. PtP_2CH derivatives

There are over thirty derivatives with PtP_2CH inner coordination sphere. These complexes crystallized in three crystal systems: orthorhombic (×4), triclinic (×6) and monoclinic (×23). In twenty one complexes of the composition: $[Pt(PEt_3)_2(H)(CL)]$: (CL) = $\{C_9H_8N_2\}$ [15], $\{C_9H_9N_4\}$ [16]; $[Pt(PPr^i_3)_2(H)(Ph)]$ [17], $[Pt(PPr_3)(H)(adpo)]$ [18], $[Pt(PBu^t_2Bu)_2(H)(MeOOCC = CHCOOMe)]$ [19]; $[Pt(PPh_3)_2(H)(CL)]$: (CL) = $\{CH_2CN\}$ [20], $\{COCH_2CH_2O\}{\cdot}(BF_4)$ [21], $\{CF_3\}$ (at 180 K) [21] and (at room temperature) [22], $\{C{\equiv}CC(OH)(Me)(Et)\}$ [23], $\{C_6H_4F\text{-}p\}$ [24], $\{CHC(CO_2CF_3)_2\}$ [25], $\{C{\equiv}CPh\}$ [26] $\{C{\equiv}CC_6H_4CN\text{-}p\}$ [27]; $Pt(Pcy_3)_2(H)\{CL\}]$: $\{CL\}$ = $\{C(CHO)CO\}$ monoclinic [28] and orthorhombic [29], $\{C(CHO)C(O)N(H)Ph\}$ [30], {hfba} [31], $\{C_5H_8N_2\}(BF_4)$ monoclinic and triclinic [32] and $\{C_5F_4N\}$ [33] only monodentate ligands involved and created trans-configuration.

The mean Pt-P bond distance elongated in the order: 2.275 Å (PPr_3) < 2.276 Å (PPh_3) < 2.279 Å (PEt_3) < 2.286 Å (Pcy_3) < 2.302 Å (PBu^t_3). The mean Pt-C bond distance (trans to H) elongated in the order: 1.91 Å (CF_3) < 2.08 Å (CL) < 2.10 Å (Ph) < 2.16 Å (CH_2CN). The mean Pt-H bond distance is 1.73 Å. The mean Pt-P and Pt-C bond distances are 2.282 and 2.06 Å. The mean values of *cis*-L-Pt-L bond angles are 85.8° (H-Pt-P) and 97.6° (C-Pt-P) and mean *trans*-L-Pt-L bond angles are 166.7° (P-Pt-P) and 169.1° (H-Pt-C).

In colorless monoclinic *cis*-$[Pt\{\eta^2\text{-}Bu^t_2PCH_2PBu^t_2\}(H)(hydridoneopentyl)]$ [34] the chelating-P,P′ donor ligand forms four-membered metallocyclic ring with P-Pt-P bite angle of 74.7(1)°. In another seven *cis*-complexes: $[Pt\{\eta^2\text{-}Pr^i_2P(CH_2)_2PPr^i_2\}(H)(CN)]$ [35], $[Pt\{\eta^2\text{-}Pr^i_2P(CH_2)_2PPr^i_2\}(H)(C_6H_4CN\text{-}2)]$ [35], $[Pt\{\eta^2\text{-}Bu^t_2P(CH_2)_2PBu^t_2\}(H)(CNhexyl)]PF_6$ [36a], $[Pt\{\eta^2\text{-}Bu^t_2P(CH_2)_2PPh_2\}(D)(C_6D_5)]$ [36b], $[Pt\{\eta^2\text{-}cy_2P(CH_2)_2Pcy_2\}(H)(hydridoneopentyl)]$ [37], $[Pt\{\eta^2\text{-}cy_2P(CH_2)_2Pcy_2\}(H)(C_6F_5)]$ [38] and $[Pt\{\eta^2\text{-}Ph_2P(CH_2)_2PPh_2\}(H)(C_3F_7)]$ [39] each chelating-P,P′donor ligand forms five-membered metallocyclic ring with the mean value of P-Pt-P bite angle of 88.0° (PC_2P). In colorless monoclinic *cis*-$[Pt\{\eta^2\text{-}cy_2P(CH_2)_3Pcy_2\}(H)(m\text{-tolyl})]{\cdot}toluene$ (Fig. 2) [40] the chelating ligand forms six-membered metallocycle with the value of P-Pt-P bite angle of 93° (PC_3P). The chelating-P,P′donor ligands coordinated unsymmetrically with the mean values of Pt-P bond distances of 2.275 Å (trans to C) and 2.322 Å (trans to H) as a reason of somewhat stronger effect of H over C. The mean values of the remaining *cis*-L-Pt-L bond angles open in the sequence: 88.4° (H-