

Stereochemistry of Platinum Organometallics

Milan Melník*^a and Ján Garaj^a, and Clive Eduard Holloway^b

^aDepartment of Natural Sciences, Alexander Dubcek University in Trencin, Studentska 1, 812 50 Trencin, Slovak Republic

^bDepartment of Chemistry, York University, 4700 Keele st., North York M 3J, 1P3, Ontario, Canada

Abstract: The organometallic chemistry of platinum covers a huge field, as shown by a recent survey covering the crystallographic and structural data of almost one thousand organometallic derivatives. About nine percent of those derivatives exist as isomers and are summarized in this review and include distortion (90 %), cis - trans (6%) and ligand isomerism (4%). These are discussed in terms of the coordination about the platinum atom, and correlations are drawn between donor atom, bond length and interbond angles, with attention to any trans - effect.

Distortion isomers, differing only by degree of distortion in Pt-L bond lengths and L- Pt -L bond angles, are the most numerous. They are also spread over a wider range of oxidation states of platinum, (zero, +1, +2, +4, mixed valence +1 plus +2 and +2 plus +4), compared to cis-trans and ligand isomerism in which only +2 is found.

Keywords: Pt, Stereochemistry, X-ray, Isomerisms, Distortion, Cis-, Trans-, Ligand.

1. INTRODUCTIONS

The organometallic chemistry of platinum covers a vast range of compounds as shown by a recent survey covering the crystallographic and structural data of almost one thousand examples [1-4]. Systematic studies in the field of stereoselectivity of complexes over the last 50 years have become of increasing interest since this is very often related to important stereospecificity of biological systems, and the catalysis and stereochemical effects in technical processes. Isomers can be broadly classed into two major categories, structural and stereoisomers. The former can be divided into: ionization, hydrate, coordination, linkage and polymerization sub-categories. The latter can be divided into geometric (cis-trans, fac-mer), optical, ligand and distortion isomerism.

Recently [5] we analyzed and classified over two hundred isomeric examples of platinum monomeric coordination complexes about sixty five percent of which are distortion isomers, about 30% cis – trans and the remainder mixed isomers (cis-trans plus distortion) and ligand isomerism. Distortion isomers, differing only by degree of distortion in Pt–L distances and L-Pt-L angles, are by far the most numerous.

In this review we analyze and classify isomers of platinum organometallic complexes, to show that stereoisomers are more common than structural isomers, and, surprisingly, that distortion isomerism is again more common than the better known cis – trans isomerism. The aim of this manuscript is to discuss the factors which could lead to a better understanding of stereochemical interaction within the coordination sphere of platinum organometallic compounds, and to examine some cooperative effects between isomeric types.

The system has been classified according to the coordination number of the platinum, and further subdivided in each

group into monomers and oligomers. The compounds have been listed and referenced in order of increasing coordination number, increasing complexity of the coordination sphere, and increasing atomic number of the principal coordinating ligand. Where the oxidation number for a platinum atom is not designated, it may be taken to be platinum(II).

2. DISTORTION ISOMERISM

The coexistence of two or more species differing only by degree of distortion of M-L bond distances and L-M-L bond angles is typical of the general class of distortion isomers [6]. There are almost one hundred examples in the chemistry of platinum organometallic compounds. The platinum oxidation states in these isomers are found in the oxidation states of zero, +1,+2 (the most common) and + 4.

2.1. Mononuclear Complexes

2.1.1. Isomeric Forms

Crystallographic and structural data for mononuclear platinum organometallic compounds which exist in two [7-36] and even three [37] isomeric forms are gathered in Table 1. Colourless Pt(PPh₃)₃CO, monoclinic [7] and rhombohedral [8] are the only examples of a pair of Pt(0) distortion isomers. The isomers consist of three bulky unidentate PPh₃ ligands and CO ligand in an approximately tetrahedral geometry about each Pt(0) atom.

There are thirty six Pt(II) [10-34] and one Pt(IV) [35,36] distortion isomers which exist in two isomeric forms with homo- as well as hetero- crystal classes and pale yellow [Pt(η-CH₂Cl)(η³-tmba)Cl] [37] exists in three monoclinic isomeric forms (Table 1).

In twelve derivatives both isomeric classes belong to the homo-monoclinic [11, 21-28], orthorhombic [18], triclinic [19,20] and tetragonal[35,36]. The remaining examples differ from each other not only by degree of distortion but also by crystal class. In twelve of these one isomer is monoclinic and the other orthorhombic [9,13,14,29-33]. In two examples

*Address correspondence to this author at the Department of Natural Sciences, Alexander Dubcek University in Trencin, Studentska 1, 812 50 Trencin, Slovak Republic; Tel: +421 2 52495239; Fax: +421 2 52493198; E-mail: milan.melnik@stuba.sk

Table 1. Crystallographic and Structural Data for Mononuclear Platinum Organometallic Compounds – Distortion Isomers^a

| COMPOUND (colour) | Cryst. cl. SPACE GR. Z | a[Å] b[Å] c[Å] | | | Chromo- PHORE | Pt – L [Å] | | L – Pt – L [°] | | Ref. |
|--|------------------------------|---|--|------------------------------------|---------------------------------|--------------------------------------|------------------------------------|----------------------------|---|------|
| | | α [°] β [°] γ [°] | | | | | | | | |
| Pt ⁰ (PPh ₃) ₃ (CO) (colourless) | m P2 ₁ /n 4 | 11.275(5) 30.904(8) 13.298(5) | | 91.6(1) | PtP ₃ C | Ph ₃ P ^b OC | 2.334(8,1) 1.86(3) | P,P ^b P,C | 111.4(3,2,3) 107(1,2) | [7] |
| Pt ⁰ (PPh ₃) ₃ (CO) (colourless) | rh P3 3 | 19.01(1) 10.780(5) | | | PtP ₃ C | | not given | | not given | [8] |
| cis-Pt(Me) ₂ (MeNC) ₂ (colourless) | m C2/c 8 | 26.584(2) 6.062(1) 11.318(1) | | 108.038(7) | PtC ₄ | MeC MeNC | 2.065(30,5) 1.99(2,3) | C,C | 90.0(9,5,3) 174.2(9,9) | [9] |
| cis-Pt(Me) ₂ (MeNC) ₂ (colourless) | or Pbcn 8 | 25.313(1) 6.0161(7) 11.375(1) | | | PtC ₄ | MeC MeNC | 2.062(8,6) 1.966(8,13) | C,C | 90.0(3,3,9) 175.6(3,8) | [9] |
| Pt(η^2 -C ₈ H ₄ O ₂)(PPh ₃) ₂ (red) | m P2 ₁ /c 4 | 11.79 22.27 15.64 | | 122.0 | PtC ₂ P ₂ | | | | | [10] |
| Pt(η^2 -C ₈ H ₄ O ₂)(PPh ₃) ₂ (blue) | tr P-1 2 | 9.740 9.797 19.610 | | 99.9 96.9 105.6 | PtC ₂ P ₂ | | | | | [10] |
| Pt{ η^2 -CH ₂ C ₆ H ₄ PBu ^t (o-tolyl)} ₂ (colourless) | m P2 ₁ /n 2 | 12.59(2) 10.69(2) 12.44(2) | | 103.7(1) | PtC ₂ P ₂ | η^2 C η^2 P | 2.15(2) 2.238(4) | C,P | 82.6(6) ^c | [11] |
| Pt{ η^2 -CH ₂ C ₆ H ₄ PBu ^t (o-tolyl)} ₂ (colourless) | m C2/c 4 | 11.98(1) 17.63(2) 15.39(2) | | 97.0(1) | PtC ₂ P ₂ | η^2 C η^2 P | 2.08(3) 2.295(6) | C,C P,P C,P | 84.1(9) 109.5(2) 83.3(7) ^c | [11] |
| Pt(SMe ₂) ₂ (Ph)Cl (pale yellow) | tr P-1 2 | 7.9076(6) 8.994(6) 9.998(1) | | 85.88(1) 80.600(9) 76.668(7) | PtS ₂ CCl | S PhC Cl | 2.293(2,4) 2.004(5) 2.420(1) | S,S C,Cl S,C S,Cl | 178.51(5) 179.9(1) 89.5(1,4,5) 90.5(1,4,6) | [12] |
| Pt(SMe ₂) ₂ (Ph)Cl ^d (pale yellow) | m P2 ₁ /n 8 | 10.106(1) 13.046(3) 20.939(3) | | 94.39(1) | PtS ₂ CCl | S PhC C | 2.295(4,4) 1.99(1) 2.404(3) | S,S C,Cl S,C S,C | 170.8(1) 177.7(4) 85.7(4,3) 94.4(1,6) | [12] |
| | | | | | PtS ₂ CCl | S PhC C | 2.287(4,8) 1.99(1) 2.403(4) | S,S C,Cl S,C S,C | 171.9(1) 177.2(3) 86.0(4,2) 94.1(1,1,1) | |
| Pt(Pcy ₃) ₂ (H){ η -C(CHO)(CO)} | m P2 ₁ /a 4 | 19.404(9) 11.889(6) 18.534(9) | | 91.3(1) | PtP ₂ HC | P H η C | 2.284(3,3) not given 2.14(1) | P,P | 165.4(2) | [13] |

(Table 1). Contd.....

| | | | | | | | | | |
|--|--|--------------------------------------|------------------------------------|----------------------------------|--|--|----------------------------|---|------|
| Pt(Pcy ₃) ₂ (H){η-C(CHO)(CO)} (pale yellow) | or Fdd2 8 | 31.204(14) 15.449(6) 18.467(8) | | PtP ₂ HC | P H ηC | 2.291(3,0) not given 2.08(1) | P,P P,C | 164.0(3) 98.3(4) | [14] |
| Pt(PMe ₃) ₂ (η-hfp)(Me) (white) | m P2 ₁ /a 4 | 12.056(3) 16.938(3) 9.156(3) | 104.91(2) | PtP ₂ OC | Me ₃ P MeC ηO | 2.181(4) 2.317(4) 2.13(2) 2.07(1) | P,P O,C P,O P,C | 101.6(2) 89.6(5) 80.6(3) 171.6(3) 88.3(5) 169.7(5) | [15] |
| [Pt(PMe ₃) ₂ (η-hfp)(Me)].hfpH (white) | trg P3 ₁ 3 | 9.347(6) 23.317(3) | | PtP ₂ OC | Me ₃ P MeC ηO | 2.199(8) 2.334(8) 2.07(3) 2.06(3) | P,P O,C P,O P,C | 96.9(3) 86(1) 88.0(7) 175.0(7) 89(1), 174(1) | [16] |
| Pt(η ³ -bdpep)Cl (white) | or Pbca 8 | 21.807(3) 17.020(5) 16.519(2) | | PtP ₂ CCl | η ³ P η ³ C Cl | 2.261(6,8) 2.200(2) 2.368(6) | P,P C,Cl P,C P,Cl | 163.4(2) 178.5(5) 81.7(6,5) ^c 98.3(2,8) | [17] |
| [Pt(η ³ -bdpep)Cl].CHCl ₃ (white) | m P2 ₁ /c 4 | 11.850(2) 15.150(3) 19.837(2) | 98.69(1) | PtP ₂ CCl | η ³ P η ³ C Cl | 2.271(2,3) 2.003(9) 2.384(2) | P,P C,Cl P,C P,Cl | 163.1(1) 177.6(3) 81.8(3,6) ^c 98.3(1,1) | [17] |
| Pt(η ³ -hxmba)Cl ₂ (colourless) | or P2 ₁ 2 ₁ 2 ₁ 3 | 16.21 12.23 8.01 | | PtC ₃ Cl ₂ | η ³ C Cl | 2.05(2) 2.11(2,1) 2.339 2.433 | Cl,Cl C,Cl | 89.3(1.0) 89.7(1.0) 178.6(1.0) | [18] |
| Pt(η ³ -hxmba)Cl ₂ (colourless) | or P2 ₁ 2 ₁ 2 ₁ 3 | 23.53 7.49 8.69 | | PtC ₃ Cl ₂ | η ³ C Cl | 2.05(2) 2.11(2,1) 2.334 2.430 | Cl,Cl C,Cl | 90.8(1.0) 86.9(1.0) 174.7(1.0) | [18] |
| [Pt{η ³ -CH ₂ C(SPh)CH ₂ }. (PPh ₃) ₂]BF ₄ CHCl ₃ (pale yellow) | tr P-1 2 | 12.842(3) 12.989(3) 13.589(5) | 89.85(2) 92.98(3) 106.66(2) | PtC ₃ P ₂ | η ³ C Ph ₃ P | 2.177(6,0) 2.204(6) 2.290(2,4) | C,C P,P C,P | 37.1(2,5) ^e 66.9(2) 101.90(6) 95.3(2,2.8) 128.6(2,1.9) 161.3(2,2.9) | [19] |
| [Pt{η ³ -CH ₂ C(SPh)CH ₂ }. (PPh ₃) ₂]BF ₄ CHCl ₃ (pale yellow) | tr P-1 2 | 11.285(3) 11.615(2) 17.946(2) | 106.57(1) 91.44(1) 106.43(2) | PtC ₃ P ₂ | | | | | [20] |
| (PPh ₄)[PtCl ₃ (η ² -C ₄ H ₈ O ₂)] (yellow) | m P2 ₁ /c 4 | 13.665 7.471 27.402 | 102.08 | PtCl ₃ C ₂ | Cl η ² C | 2.296(9,5) 2.14(3,4) | Cl,Cl C,C | 88.8(3,4) 177.3(4) 38.1(9) ^e | [21] |
| (NEt ₄)[PtCl ₃ (η ² -C ₄ H ₈ O ₂)] (pale yellow) | m P2 ₁ /n 4 | 7.728(4) 17.763(6) 13.418(9) | 103.71(1) | PtCl ₃ C ₂ | Cl η ² C | 2.300(2,8) 2.324(2) 2.128(7) 2.208(7) | Cl,Cl C,C Cl,C | 90.0(1,8) 179.2(9) 37.1(3) ^e 161.5(3,4,3) | [22] |

(Table 1). Contd.....

| | | | | | | | | | |
|--|--|-------------------------------------|------------|------------------------------------|--|--|--------------------------|---|------|
| PtCl ₃ (η ² -C ₄ H ₁₀ N-2) (orange yellow) | m P2 ₁ /c 4 | 10.248(3) 10.388(1) 8.414(1) | 97.96(2) | PtCl ₃ C ₂ | Cl η ² C | 2.298(7,10) 2.339(7) 2.14(3,2) | Cl,Cl C,C | 89.0(3,6) 177.2(2) 38.1(10) ^o | [23] |
| PtCl ₃ (η ² -C ₄ H ₁₀ N-2) (yellow) | m P2 ₁ /c 4 | 7.2254(4) 7.521(1) 16.596(1) | 92.77(2) | PtCl ₃ C ₂ | Cl η ² C | 2.297(6,4) 2.320(6) 2.165(20,15) | Cl,Cl C,C | 88.8(3,2) 177.5(2) 37.8(10) ^o | [24] |
| PtCl ₃ (η ² -C ₃ H ₁₂ N-4) (yellow) | m P2 ₁ /c 4 | 6.435(1) 9.372(11) 16.737(13) | 100.6(1) | PtCl ₃ C ₂ | Cl η ² C | 2.321(9,0) 2.335(9) 2.182(30,12) | Cl,Cl C,C | 89.2(3,1.3) 177.5(3) 37.6(10) ^o | [25] |
| PtCl ₃ (η ² -C ₃ H ₁₂ N-4) (orange) | m P2 ₁ /c 4 | 10.504(7) 10.627(10) 9.608(8) | 106.9(1) | PtCl ₃ C ₂ | Cl η ² C | 2.301(6,13) 2.342(6) 2.129(23,19) | Cl,Cl C,C | 89.7(2,9) 175.2(2) 38.8(8) ^o | [25] |
| PtCl ₃ (η ² -C ₃ H ₁₂ N-2) (yellow) | m P2 ₁ /c 4 | 11.215(3) 8.729(2) 10.259(3) | 90.01(1) | PtCl ₃ C ₂ | Cl η ² C | 2.314(5,2) 2.321(4) 2.097(14) 2.183(14) | Cl,Cl C,C | 88.4(1,4) 174.5(1) 38.1(5) ^o | [26] |
| PtCl ₃ (η ² -C ₃ H ₁₂ N-2) (yellow) | m P2 ₁ /c 4 | 10.530(3) 9.037(3) 10.067(3) | 105.50(3) | PtCl ₃ C ₂ | Cl η ² C | 2.306(3,1) 2.330(7) 2.156(13,10) | Cl,Cl C,C | 89.1(1,1.0) 174.3(1) 37.9(4) ^o | [27] |
| [PtCl ₃ (η ² -C ₄ H ₁₂ N ₂)]Cl (yellow) | m P2 ₁ /c 4 | 11.238(3) 13.234(4) 7.769(1) | 112.99(2) | PtCl ₃ C ₂ | Cl η ² C | 2.305(4,4) 2.330(4) 2.134(15,2) | Cl,Cl C,C | 89.0(2,5) 177.7(2) 39.5(6) ^o | [27] |
| [PtCl ₃ (η ² -C ₄ H ₁₂ N ₂)]Cl.0.5H ₂ O (yellow) | m C2/c 4 | 23.911(7) 6.942(1) 13.956(2) | 102.07(2) | PtCl ₃ C ₂ | Cl η ² C | 2.302(2,9) 2.342(2) 2.130(8,19) | Cl,Cl C,C | 88.6(1,5) 176.11(9) 38.9(3) ^o | [28] |
| PtCl ₃ (η ² -C ₅ H ₁₁ NMe) (yellow) | or Pna2 ₁ 4 | 18.623(7) 8.385(2) 7.261(2) | | PtCl ₃ C ₂ | Cl η ² C | 2.273(9,12) 2.336(2) 2.19(4) 2.24(3) | Cl,Cl C,C | 91.6(3,5) 176.7(3) 37(1) ^o | [29] |
| [Pt(Cl ₃)(η ³ -C ₅ H ₁₁ NMe)].H ₂ O (yellow) | m P2 ₁ /c 4 | 11.500(4) 6.088(4) 18.961(5) | 116.92(4) | PtCl ₃ C ₂ | Cl η ² C | 2.289(4) 2.329(4,5) 2.141(12,10) | Cl,Cl C,C | 88.8(1,6) 174.8(2) 38.2(6) ^o | [30] |
| Pt(η ² -MeCH=CHMe)Cl ₂ . (η ¹ -pea) (yellow) | m P2 ₁ 2 | 12.87(2) 6.58(1) 8.86(1) | 102.38(15) | PtC ₂ Cl ₂ N | η ² C Cl η ¹ N | 2.16(5,1) 2.32(2,3) 2.14(3) | Cl,Cl Cl,N | 89(1) 90(1) 176(1) | [31] |
| Pt(η ² -MeCH=CHMe)Cl ₂ . (η ¹ -pea) (yellow) | or P2 ₁ 2 ₁ 2 ₁ 4 | 15.64(5) 10.42(3) 9.16(3) | | PtC ₂ Cl ₂ N | η ² C Cl η ¹ N | not given 2.34(2,0) not given | Cl,Cl | 180 | [32] |
| Pt(η ⁴ -dph)Cl ₂ (pale yellow) | m C2/c 4 | 18.258(5) 8.395(3) 11.043(2) | 108.5(6) | PtC ₄ Cl ₂ | η ⁴ C Cl | 2.19(2,0) 2.30(2,0) 2.324(5,0) | C,C Cl,Cl C,Cl | 37.5(8) ^o 81.9(7,3.3) 11.0(7) 83.9(5) 101.0(4) 161.8(7) | [33] |

(Table 1). Contd.....

| | | | | | | | | | |
|--|------------------------------|------------------------------------|-----------|---|--|--|-----------------------------|--|------|
| Pt(η^4 -dph)Cl ₂ (pale yellow) | or Pbc2 ₁ 4 | 6.484(2) 20.484(5) 12.719(9) | | PtC ₄ Cl ₂ | η^4 C Cl | 2.15(4,5) 2.30(3,4) 2.292(8,14) | C,C Cl,Cl | 36.8(3,5) ^e 87.4(3) | [34] |
| Pt ^{IV} (η^2 -phen)(Me) ₂ (SePh) ₂ (orange) | tg I4 _{1/a} 8 | 13.874(3) 25.14(3) | | PtN ₂ C ₂ Se ₂ | η^2 N MeC Se | 2.143(6,0) 2.056(8,0) 2.4896(9,0) | N,N C,C Se,Se | 77.2(2) ^e 85.6(3) 174.70(3) | [35] |
| Pt ^{IV} (η^2 -phen)(Me) ₂ (SePh) ₂ (orange) | tg I4 _{1/a} 8 | 13.874(3) 25.14(3) | | PtN ₂ C ₂ Se ₂ | η^2 N MeC Se | 2.143(6,0) 2.056(8,0) 2.4896(9,0) | N,N C,C Se,Se | 77.2(2) ^e 85.6(3) 174.70(3) | [35] |
| Pt ^{IV} (η^2 -phen)(Me) ₂ (SePh) ₂ (orange) | tg I4 _{1/a} 8 | 13.918(2) 25.432(5) | | PtN ₂ C ₂ Se ₂ | η^2 N MeC Se | 2.120(18,0) 2.092(20,0) 2.495(3,3) | N,N C,C Se,Se | 75.0(7) ^e 87.4(9) 175.4(1) | [36] |
| [Pt ^{IV} (η -CH ₂ Cl)(η^3 -tmba)Cl] (pale yellow) | m P2 _{1/n} 4 | 7.578(1) 15.950(3) 10.885(2) | 107.26(2) | PtC ₃ NCl | η C η^3 C η^3 N Cl | 2.016(11) 2.127(9,9) 2.176(7) 2.310(3) | C,C C,N N,Cl C,Cl | 38.4(4) ^e 93.7(4,4,4) 82.4(3) ^e 90.8(3) 179.6(4) 92.2(2) 87.6(4) 160.7(3,1,4) | [37] |
| [Pt(η -CH ₂ Cl)(η^3 -tmba)Cl] (pale yellow) | m P2 _{1/c} 4 | 8.464(2) 9.563(2) 15.112(3) | 94.68(2) | PtC ₃ NCl | η C η^3 C η^3 N Cl | 2.057(13) 2.251(15,4) 2.086(9) 2.301(3) | C,C C,N N,Cl Cl,Cl | 34.9(5) ^e 162.5(5,4,9) 83.3(4) ^e 92.7(5,1,9) 175.1(3) 90.3(4,3,9) | [37] |
| [Pt(η -CH ₂ Cl)(η^3 -tmba)Cl] (pale yellow) | m P2 _{1/n} 4 | 6.575(2) 12.141(2) 16.129(3) | 101.10(2) | PtC ₃ NCl | η C η^3 C η^3 N Cl | 2.03(2) 2.13(2,0) 2.18(1) 2.318(5) | C,C C,N N,Cl Cl,Cl | 37.0(4) ^e 94.2(4,2,8) 83.1(3) ^e 89.4(3) 178.7(3) 92.5(2) 87.2(3) 161.4(3,4,2) | [37] |

Footnotes: a.) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b.) The chemical identity of the coordinated atom or ligand is specified in these columns.

c.) Five-membered metallocyclic ring.

d.) There are two crystallographically independent molecules.

e.) Three membered metallocyclic ring.

one is monoclinic and the other triclinic [10,12]. For the remainder, the mixture is monoclinic and trigonal [15,16].

There is an example, [Pt(SMe₂)₂(Ph)(Cl)] [12] which exists in two isomeric forms where one form contains two crystallographically independent molecules.

Each Pt(II) atom with the chromophores: PtC₄, PtC₂P₂, PtS₂CCl, PtP₂HC, PtP₂OC and PtP₂CCl has a square-planar arrangement with a different degree of distortion [9-17]. The remaining Pt(II) examples with the chromophores: PtC₃X₂ (X = Cl [8] or P [19, 20]), PtCl₃C₂ [21 - 30] and PtC₂Cl₂N

[31, 32] and PtC₄Cl₂ [33, 34] are a π - complexes. Each Pt(II) atom (PtC₃X₂) is found in the square-planar arrangement with two X in cis - position. The one C atom σ - bonded to the Pt atom (Pt - C, 2.40 Å average) and the center of the doubled bond (Pt - C, \approx 2.10 Å of the respective tridentate C donor atoms ligand, occupy the other sites of coordination. Each Pt(II) atom in PtCl₃C₂ [21 - 30] is square coordinated with three chlorine atoms and the double bond of the respective ligand. In Pt(η^4 -dph)Cl₂ monoclinic [33] and orthorhombic [34] a square planar geometry about each Pt(II) atom is built up by two chlorine atoms in cis- position

and two centers of double bond of the 2,5 – diphenyl-1,5-hexadiene ligand.

Each Pt(IV) atom in Pt(η^2 -phen)(Me)₂(SePh)₂ [35, 36] is a tetragonal -bipyramidally coordinated (PtN₂C₂Se₂) with Se atom in the axial positions with Se – Pt – Se bond angles of 174.6° (average).

As mentioned above, pale yellow [Pt(η -CH₂Cl)(η^3 -tmba)Cl] [37] exists in three monoclinic isomeric form and one example structure is shown in (Fig. 1). In all three molecules the five membered ring Pt, N, C(1), C(2), C(3) has a C(2) envelope conformation, with the Pt, C(3), C(4) plane inclined at 101.4, 98.9 and 102.9°, respectively to the coordination plane Pt, N, C(1), C(9). Otherwise, the bond lengths and angles are not unusual (Table 1).

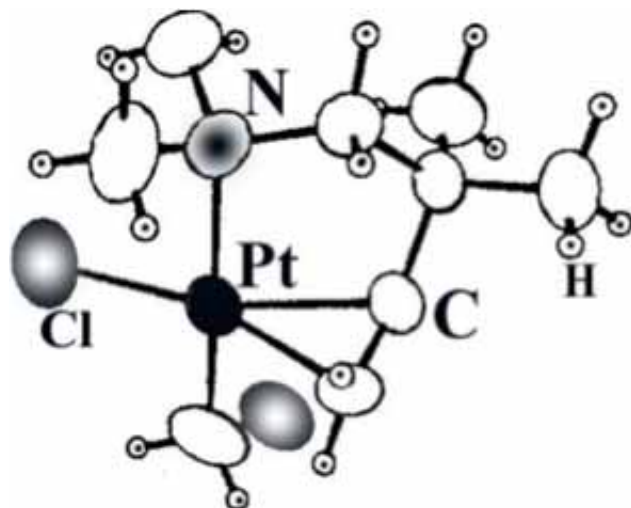


Fig. (1). Structure of one isomeric form of [Pt^{II}(η -CH₂Cl)(η^3 -tmba)Cl] [37].

2.1.2. Crystallographically Independent Molecules

Crystallographic and structural parameters of monomeric platinum organometallic compounds contain two, three and four crystallographically independent molecules within the same crystal are given in Table 2. There are thirty six derivatives, which contain two crystallographically independent molecules within the same crystal [12, 37-71]. One derivative contains three such molecules [72] and another one derivative has four such molecules [73]. In these derivatives the platinum atoms are found in the oxidation states of zero (x5) [38-42], +2 (x 27) [12, 37, 43-65, 72, 73] and +4 (x 6) [66-71]. The derivatives belong to the triclinic (x 17), monoclinic (x 16) and orthorhombic (x 5) classes.

In pale yellow Pt(η^2 -bchp)₂ [38] the pair of homobidentate bchp ligands (C, C'-donors) with two three – membered rings creating a distorted tetrahedral geometry about the Pt(0) atom (PtC₄) with differing degrees of distortion. The mean Pt – C bond distances are 1.99 Å (molecule 1) and 2.01 Å (molecule 2).

In another three Pt(0) derivatives Pt(η^2 -CL)(PPh₃)₂ (CL is HC=C₆H₁₀OH [39], had [40] and bcn [41] a homobidentate (C, C'- donors) ligand and two PPh₃ ligands create a tetrahedral arrangement about each Pt(0) atom (PtC₂P₂), with differing degrees of distortion. In Pt⁰(η^2 -sti)(η^2 -chirophos) [42] a homobidentate sti (C, C'- donors and chirophos (P,P'-donors) ligands form two metallocycles, three - and five –

membered, with the mean C – Pt – C and P – Pt – P bite angles of 39.3(2)°, and 87.13(6)° (molecule 1), and 39.9(3)° and 86.55(6)° (molecule 2).

The overall data (Table 2) shows that there are twenty two Pt(II) derivatives in which each Pt(II) atom has a square planar geometry with different degrees of distortion. There is wide variety of the chromophores: PtN₃C [43], PtN₂C₂ [44], PtC₂P₂ [45-47], PtN₂CX (X = Cl [48, 49] or P [50]), PtC₂NX (X = Cl [51] or I [52]), PtCl₂NC [53, 54], PtS₂CCl [12], PtP₂HC [55], PtP₂CX (X = Cl [56, 57] or I [58]), [PtNCCIP [59, 60], PtCCISP [61] and PtNCSAs [73].

Remaining Pt(II) derivatives with the chromophores about the Pt(II) atoms: PtC₃X₂ (X = Cl [37] or P [62]), PtC₂Cl₂N [63], PtC₄NS [64] and PtC₃CIP [72] are π -complexes. Each Pt(II) atom is square coordinated.

The structure of dark red [Pt(η^2 -PhC≡CPh)(η^2 -dmphen)I₂].CHCl₃ [65] contains two crystallographically independent molecules, of which one is shown in (Fig. 2), and disordered chloroform molecule. Each complex has a crystallographically imposed C_s and an approximate C_{2v} symmetry with the mirror plane bisecting the dmphen and the diphenylacetylene moieties and comprising the PtI₂ fragment. The platinum(II) atom exhibits a tetragonal bipyramidal coordination. In the axial positions are iodides atoms and the equatorial sites are occupied by the two nitrogen atoms of the bidentate dmphen ligand and by carbon atoms of diphenylacetylene (PtN₂C₂I₂).

In six Pt(IV) derivatives [Pt(η^2 -bpy)(η^2 -mq)(Me)₂]BF₄ [66], [Pt(η^2 -htpzb)(Ph)₂(I)₂(I)₂(I)₃] [67], Pt(CH₂Ph)(η^2 -thpy)₂Br [68], [Pt(Me)₃(η^2 -dmpbpy)I] [69], [Pt(py)₂{ η^2 -C₃H₄(Ph)₂}Cl₂] [70] and [Pt(Me)₃(η^2 -C₃H₃NP₂)I] [71] each Pt(IV) atom is octahedrally coordinated: PtN₃C₃ [66], PtN₃C₂I [67], PtC₃N₂X (X = Br [68] or I [69]), PtN₂C₂Cl₂ [70] and PtC₃NPI [71], with different degrees of distortion (Table 2).

2.2. Bi -, Tri- and Tetranuclear Complexes

There are eleven binuclear [74-83], three trinuclear [84-86] and three tetranuclear [87-89] derivatives which contain two crystallographically independent molecules within the same crystal and their structural parameters are given in Table 3.

Yellow Pt₂(μ -S)(CO)₂(PPh₃)₂ [74] is only example with Pt(I). In each dimer, the (PPh₃)(CO)Pt-Pt(CO)(PPh₃) unit with Pt(I) – Pt(I) bond distances of 2.5998(8) and 2.6008(8) Å, is bridged by a single μ -S atom. The Pt – S – Pt bridge angles are 70.1(1) and 70.2(1)°, respectively.

In pale orange derivative [Pt₂(μ -C=CHPh)(PEt₃)₃] [75] non-equivalent fragments, (PEt₃)(Br)Pt and Pt(Br)(PEt₃)₂, are both bridged unsymmetrically by a μ -C=CHPh ligand and linked by a Pt(II) – Pt(II) bond. The Pt – Pt bond distances are 2.682(1) and 2.687(1) Å, respectively.

Structure of yellow derivative [76] consists of discrete [Pt₂(μ -H)(μ -PPh₂)(Ph)(PPh₃)₃]⁺ cations and BF₄⁻ anions. The Pt(II) – Pt(II) bond distances are 2.889(2) Å (molecule 1) and 2.912(3) Å (molecule 2). In each of the molecules, the Pt(II) atoms are in essentially square – planar arrangement, one with PtP₃H and the other with PtP₂HC chromophores.

Table 2. Crystallographic and Structural Data for Mononuclear Platinum Organometallics which Contain Crystallographic Independent Molecules^a

| COMPOUND (colour) | Cryst. cl. SPACE GR. Z | a[Å] b[Å] c[Å] | α [°] β [°] γ [°] | Chromo- PHORE | Pt – L | | L – Pt – L | | Ref. |
|---|------------------------------|---------------------------------------|---|---------------------------------|--|---|-------------------|---|------|
| | | | | | | [Å] | | [°] | |
| Pt ⁰ (η^2 -bchp) ₂ (pale yellow) (at 183(2) K) | m C2/c 16 | 15.739(5) 15.023(5) 41.998(9) | ? | PtC ₄ | η^2 C ^b | 1.98(2,2) 2.00(2,1) | C,C ^b | not given | [38] |
| | | | | PtC ₄ | η^2 C | 1.98(2,8) 2.03(2,1) | | not given | |
| Pt ⁰ (η^2 -HC≡CC ₆ H ₁₀ OH)(PPh ₃) ₂ (pale yellow) | tr P-1 2 | 17.72(2) 17.44(2) 12.78(1) | 97.8(1) 101.6(1) 86.9(1) | PtC ₂ P ₂ | η^2 C Ph ₃ P | 2.083(13,14) 2.302(4,4) | C,C P,P C,P | 36.4(4) ^c 109.3(1) 107.3(4,6.3) | [39] |
| | | | | PtC ₂ P ₂ | η^2 C Ph ₃ P | 2.064(15,3) 2.294(4,7) | C,C P,P C,P | 37.4(5) ^c 108.0(1) 107.3(4,3.1) | |
| Pt ⁰ (η^2 -had)(PPh ₃) ₂ ^d (colourless) | tr P-1 4 | 21.002(9) 15.117(5) 12.035(3) | 97.83(2) 94.81(3) 97.27(3) | PtC ₂ P ₂ | η^2 C Ph ₃ P | 2.055(14,13) 2.258(3,2) | C,C P,P | 37.3(5) ^c 108.8(1) | [40] |
| Pt ⁰ (η^2 -bcn)(PPh ₃) ₂ ^d (pale yellow) | tr P-1 2 | 11.34(1) 11.90(2) 16.14(1) | 79.4(1) 70.4(1) 67.2(1) | PtC ₂ P ₂ | η^2 C Ph ₃ P | 2.11 2.16 2.28(-,2) | | not given | [41] |
| Pt ⁰ (η^2 -sti)(η^2 -chirophos) (yellow) (at 223 k) | or I222 16 | 16.840(2) 25.4756(3) 37.1463(3) | | PtC ₂ P ₂ | η^2 P ^p η^2 P | 2.138(5,1) 2.275(2,3) | C,C P,P C,P | 39.3(2) ^c 87.13(6) ^e 117.0(2,1.4) 155.8(2,3.5) | [42] |
| | | | | PtC ₂ P ₂ | η^2 p η^2 P | 2.122(6,4) 2.273(2,2) | C,C P,P C,P | 39.9(3) ^c 86.55(6) 116.9(2,3) 156.5(2,4) | |
| [Pt(η^3 -dpp)(MeCN)]ClO ₄ (yellow) | tr P-1 2 | 13.322(3) 13.877(3) 14.164(6) | 86.74(3) 105.87(3) 108.93(2) | PtN ₃ C | η^3 N η^3 C η^1 N | 1.940(8) 2.231(8) 2.00(1) 1.970(9) | N,N N,C | 78.6(3) ^e 107.8(3) 173.2(3) 81.4(4) ^e 92.2(4) 159.8(4) | [43] |
| | | | | PtN ₃ C | η^3 N η^3 C η^1 N | 1.918(8) 2.193(8) 1.97(1) 1.981(8) | N,N N,C | 79.3(3) ^e 103.7(3) 175.1(5) 81.6(4) ^e 95.6(4) 160.6(4) | |
| [Pt(η^2 -bpy)(COMe) ₂]H(PF ₆) (orange) (at 220(2) K) | m P2 ₁ /a 4 | 21.147(6) 14.355(2) 23.036(4) | 116.78(2) | PtN ₂ C ₂ | η^2 N C | 2.121(7,11) 1.99(1,3) | N,N | 77.0(3,4) ^e | [44] |

(Table 2).contd.....

| | | | | | | | | | |
|---|-------------------|-------------|------------|---------------------------------|--------------------------------|--|----------------------------|--|------|
| | | | | PtN ₂ C ₂ | η^2 N C | 2.128(7,14) 1.98(1,4) | N,N | 76.3(3,3) ^e | |
| cis-Pt(C≡CPh) ₂ (PPh ₃) ₂ (colourless) | tr | 15.25(1) | 88.9(1) | PtC ₂ P ₂ | C | 2.07(3,3) | C,C | 86(1) | [45] |
| | P-1 | 15.41(1) | 102.8(1) | | P | 2.32(1,2) | P,P | 98.4(3) | |
| | 2 | 21.20(1) | 119.1(1) | | | | C,P | 87.7(9,5.5) 172.2(9,5.0) | |
| | | | | PtC ₂ P ₂ | C P | 2.05(4,3) 2.33(1,4) | C,C P,P C,P | 86(1) 100.4(3) 86.7(9,2.6) 171.8(9,3.5) | |
| [Pt η^2 -C ₁₀ H ₁₄](PPh ₃) ₂ (colourless) | tr | 11.656(2) | 68.37(3) | PtC ₂ P ₂ | η^2 C | 2.110(9,5) | P,P | 103.1(1) | [46] |
| | P-1 | 16.548(2) | 79.33(3) | | P | 2.275(2,9) | | | |
| | 4 | 20.208(4) | 86.70(3) | | | | | | |
| | | | | PtC ₂ P ₂ | η^2 C P | 2.091(8,5) 2.278(2,6) | P,P | 106.2(1) | |
| [Pt(η^2 -Et)(η^2 -dbpp)](CB ₁₁ H ₁₂) (colourless) (at 190 K) | m | 17.715(5) | 90.046(13) | PtC ₂ P ₂ | η^2 EtC | 2.068(25) | C,C | 39.4(12) ^e | [47] |
| | P ₂ /c | 22.576(4) | | | P,P | 100.4(2) ^f | | | |
| | 8 | 16.466(3) | | | η^2 P | 2.274(4) 2.296(4) | C,P | 110.0(9,7.3) 149.3(9,7.1) | |
| | | | | | η^2 EtC η^2 P | 2.092(25) 2.282(21) 2.194(6) 2.257(6) | C,C P,P C,P | 41.6(9) ^e 104.8(2) ^f 106.7(6,3.0) 148.1(6,3.2) | |
| Pt(MeNH ₂) ₂ (η -dmu)Cl (pale yellow) | m | 15.736(6) | 145.55(3) | PtN ₂ CCl | N | 2.035(10,15) | N,N | 178.1(9) | [48] |
| | P ₂ /c | 11.481(6) | | | η C | 1.90(4) | C,Cl | 178.0(6) | |
| | 8 | 25.655(100) | | | Cl | 2.40(1) | N,C N,Cl | 90.4(9,1) 89.2(7,0) | |
| | | | | PtN ₂ CCl | N η C Cl | 2.125(4,25) 2.01(2) 2.38(2) | N,N C,Cl N,C N,Cl | 176.3(7) 178.0(6) 90.6(9,2) 88.5(6,1) | |
| Pt(η^3 -bubpy)Cl (orange) | m | 12.392(3) | 97.51(2) | PtN ₂ CCl | η^3 N | 1.999(7) | N,N | 79.9(3) ^e | [49] |
| | P ₂ /c | 16.188(7) | | | η^3 C | 2.117(7) | C,Cl | 97.2(3) | |
| | 8 | 14.047(4) | | | Cl | 2.000(11) 2.303(3) | N,C N,Cl | 83.8(4) ^e 163.6(4) 90.0(2) 178.6(3) | |
| | | | | PtN ₂ CCl | η^3 N η^3 C Cl | 1.937(7) 2.112(7) 2.006(11) 2.298(3) | N,N C,Cl N,C N,Cl | 80.0(3) ^e 98.4(3) 80.0(3) ^e 163.2(4) 98.2(2) 178.0(2) | |

(Table 2).contd.....

| | | | | | | | | | |
|---|------------------------------|--------------------------------------|-----------------------------------|----------------------|--------------------------------------|---|------------------------------|---|------|
| [Pt{ η^3 -C ₆ H ₅ (CH ₂ NMe ₂) ₂ -2,6}(PPh ₂)]CF ₃ SO ₃ (white) | tr P-1 4 | 12.168(1) 12.407(1) 18.676(1) | 90.78(1) 104.55(1) 94.18(1) | PtN ₂ CP | η^3 N η^3 C P | 2.104(6,2) 1.990(7) 2.346(2) | N,N C,P N,C N,P | 160.0(2) 176.8(2) 80.1(3,1) [°] 99.9(2,3.1) | [50] |
| | | | | PtN ₂ CP | η^3 N η^3 C P | 2.123(7,4) 1.961(7) 2.360(2) | N,N C,P N,C N,P | 159.9(3) 176.8(2) 80.4(3,3) [°] 99.8(2,2.0) | |
| Pt(CO)(η^2 -ctr)Cl (yellow) | m C2/c 16 | 11.5359(3) 14.644(2) 29.490(8) | 96.00(3) | PtC ₂ NCl | OC η^2 C η^2 N Cl | 1.86(1) 2.00(1) 2.07(1) 2.397(4) | C,C N,C C,Cl | 93.1(7) 80.0(5) [°] 172.7(6) 86.0(5) 175.6(4) | [51] |
| | | | | PtC ₂ NCl | OC η^2 C η^2 N Cl | 1.86(2) 2.00(2) 2.07(1) 2.407(4) | C,C N,Cl C,N C,Cl | 94.4(6) 99.6(3) 79.8(6) [°] 173.9(6) 86.4(5) 176.4(4) | |
| [Pt(C ₆ F ₅) ₂ (η^2 -ira)].0.25CHCl ₃ (yellow) | tr P-1 4 | 11.797(4) 13.735(4) 14.107(4) | 97.24(2) 90.91(2) 99.44(2) | PtC ₂ NI | C η^2 N η^2 I | 1.990(13,0) 2.132(12) 2.620(1) | C,C N,I C,N C,I | 88.4(6) 83.0(3) [°] 91.8(5) 177.2(5) 96.9(4) 174.7(4) | [52] |
| | | | | PtC ₂ NI | C η^2 N η^2 I | 1.981(13) 2.013(13) 2.128(11) 2.610(1) | C,C N,I C,N C,I | 89.0(6) 84.1(3) [°] 90.2(5) 177.9(5) 96.7(4) 174.3(4) | |
| PtCl ₂ (η -pzH)(CO) (yellow) | m P2 ₁ 4 | 3.417(1) 16.454(5) 14.571(3) | 90.60(2) | PtCl ₂ NC | Cl η N OC | 2.279(15) 2.294(14) 2.06(4) 1.78(6) | Cl,Cl N,C Cl,N Cl,C | 178.8(5) 175.8(17) 89.8(11,1.0) 90.2(1,1.6) | [53] |
| | | | | PtCl ₂ NC | Cl η N OC | 2.29(2,0) 2.11(5) 1.77(8) | Cl,Cl N,C Cl,N Cl,C | 177.0(9) 173.5(28) 88.6(14,3.7) 91.5(28,2.7) | |
| PtCl ₂ (py)(η -pyp) (yellow) | m P2 ₁ /c 8 | 11.06(2) 10.49(2) 26.01(2) | 102.65(10) | PtCl ₂ NC | Cl pyN η C | 2.30(2) 2.35(2) 2.10(6) 1.91(10) | Cl,Cl N,C Cl,N Cl,C | 179.2(9) 173(3) 89.6(17,1.3) 90.4(19,5.1) | [54] |

(Table 2).contd.....

| | | | | | | | | | |
|--|------------------------------|--------------------------------------|------------------------------------|----------------------|--|---|------------------------------|--|------|
| | | | | PtCl ₂ NC | Cl pyN ηC | 2.30(2) 2.31(2) 2.05(5) 2.11(7) | Cl,Cl N,C Cl,N Cl,C | 178.3(8) 175(2) 90.3(15,1) 89.8(20,3.7) | |
| Pt(SMe ₂) ₂ (Ph)Cl (pale yellow) | m P2 ₁ /n 8 | 10.106(1) 13.046(3) 20.939(3) | 94.39(1) | PtS ₂ CCl | S PhC Cl | 2.295(4,4) 1.99(1) 2.404(3) | S,S C,Cl S,C S,Cl | 170.8(1) 177.7(4) 85.7(4,3) 94.4(1,6) | [12] |
| | | | | PtS ₂ CCl | S PhC Cl | 2.287(4,8) 1.99(1) 2.403(4) | S,S C,Cl S,C S,Cl | 171.9(1) 177.2(3) 86.0(4,2) 94.1(1,1.1) | |
| Pt(PPr ^t) ₂ (H)(Ph) (colourless) | tr P-1 4 | 15.997(6) 19.803(5) 10.109(3) | 116.48(1) 106.28(1) 82.62(1) | PtP ₂ HC | P H PhC | 2.272(4,1) not given 2.10(2) | P,P P,C | 168.6(2) 95.5(4,6) | [55] |
| | | | | | P PhC | 2.272(5,7) 2.05(2) | P,P P,C | 169.0(2) 95.5(5,1.1) | |
| Pt(PMePh ₂) ₂ (C ₂ F ₅)Cl (colourless) | or Pna2 ₁ 8 | 15.4957(4) 9.983(3) 38.776(1) | | PtP ₂ CCl | P C Cl | 2.335(3,6) 2.013(12) 2.361(3) | P,P C,Cl P,C P,Cl | 172.1(1) 177.0(4) 93.1(3,1.9) 87.1(3,2.9) | [56] |
| | | | | PtP ₂ CCl | P C Cl | 2.333(3,7) 1.990(12) 2.365(4) | P,P C,Cl P,C P,Cl | 171.9(1) 177.8(3) 92.9(4,2.7) 87.2(1,2.7) | |
| [Pt(PPh ₃) ₂ (η- <i>ipa</i>)Cl].2/3CHCl ₃ (colourless) | tr P-1 3 | 13.357(6) 22.067(13) 11.841(8) | 95.84(8) 124.37(4) 93.15(8) | PtP ₂ CCl | Ph ₃ P ηC Cl | 2.300(5,0) 1.88(6) 2.45(1) | P,P C,Cl P,C P,Cl | 180 180 88(2) 91.1(3) | [57] |
| | | | | PtP ₂ CCl | Ph ₃ P ηC Cl | 2.298(3,2) 1.84(2) 2.361(6) | P,P C,Cl P,C P,Cl | 180 180 90.5(5,3.2) 89.6(2,1.0) | |
| Pt(PPh ₃) ₂ (η ² - <i>mppc</i>)I (pale yellow) | tr P-1 4 | 10.507(2) 15.033(2) 25.523(8) | 77.06(2) 87.77(2) 70.29(2) | PtP ₂ CI | Ph ₃ P η ² P η ² C I | 2.310(4) 2.238(5) 2.07(2) 2.645(1) | P,P C,I P,C P,I | 102.4(2) 96.1(5) 67.7(5) ^g 170.1(5) 93.8(1) 163.4(1) | [58] |
| | | | | PtP ₂ CI | Ph ₃ P η ² P η ² C I | 2.307(4) 2.228(4) 2.10(1) 2.641(1) | P,P C,I P,C P,I | 102.9(2) 96.6(4) 67.8(4) ^g 170.7(4) 92.7(1) 164.4(1) | |

(Table 2).contd.....

| | | | | | | | | | |
|--|--|-------------------------------------|----------------------------------|------------------------------------|--|--|---|---|------|
| Pt(η^2 -mbpp)(Cl)(PPr ₃) ^d (white) | m C2/c 8 | 19.653(3) 11.538(2) 18.785(2) | 107.10(1) | PtNCCIP | η^2 N η^2 C Cl Pr ₃ P | 2.179(9) 1.975(11) 2.406(3) 2.217(3) | N,C N,Cl C,P Cl,P | 69.0(4) ^g 98.8(2) 96.6(3) 95.6(1) | [59] |
| Pt(η^2 -ppy)(Cl)(Pmor ₃) ^d (yellow) (at 93 K) | m P2 ₁ /a 8 | 17.192(5) 15.593(2) 18.178(4) | 91.27(2) | PtNCCIP | η^2 N η^2 C Cl mor ₃ P | 2.106(5) 2.001(9) 2.388(2) 2.233(2) | N,C N,Cl N,P C,Cl C,P Cl,P | 80.8(2) ^e 90.7(2) 174.6(2) 168.5(2) 98.0(2) 90.04(8) | [60] |
| Pt(Me)(η^2 -ptpc)Cl ^d (colourless) | tr P-1 4 | 10.301(4) 10.986(5) 14.976(7) | 98.67(6) 92.90(6) 96.78(6) | PtCCISP | MeC Cl η^2 S η^2 P | 2.084(7) 2.365(2) 2.374(2) 2.191(2) | C,Cl C,S C,P Cl,S Cl,P S,P | 89.9(2) 177.7(2) 94.3(3) 88.9(1) 175.6(1) 87.0(1) ^g | [61] |
| Pt(η^3 -dmps)Cl ₂ (colourless) | m P2 ₁ /c 8 | 12.831(1) 12.950(1) 16.206(2) | 108.14(1) | PtC ₃ Cl ₂ | η^3 C Cl | 1.99(2) 2.13(3,2) 2.286(7) 2.386(3) | C,C Cl,Cl C,Cl | 36.7(7) ^c 92(1,1) 90.6(3) 88.3(7,2.1) 161.5(7,1.2) 177.3(6) | [37] |
| | | | | PtC ₃ Cl ₂ | η^3 C Ph ₃ P | 2.102(1) 2.15(2,3) 2.323(5) 2.407(2) | C,C Cl,Cl C,Cl | 40.1(7) ^c 92.9(8,1.4) 91.1(2) 87.9(6,1.6) 160.0(6,4.2) 179.4(6) | |
| [Pt{ η^2 -CH ₂ C(C(CO ₂ Me) ₂). CHPh}(PPh ₃) ₂]tol.0.5thf (pale yellow) | m P2 ₁ /n 4 | 12.750(2) 18.503(4) 39.658(6) | 94.69(1) | PtC ₃ Cl ₂ | η^3 C Ph ₃ P | 2.136(11,10) 2.348(10) 2.2709(3) 2.307(2) | C,C P,P C,P | 37.1(4,4) ^c 65.9(4) 100.31(9) 97.0(3,3.3) 127.7(3,4.4) 162.6(3,3.2) | [62] |
| | | | | PtC ₃ P ₂ | η^2 C Ph ₃ P | 2.148(10,2) 2.352(9) 2.280(3) 2.311(2) | C,C P,P C,P | 37.6(3,2) ^c 66.3(2) 99.19(9) 97.3(3,3.2) 127.7(2,3.7) 163.5(3,3.3) | |
| Pt(η^2 -CH ₂ =CH ₂)(Cl) ₂ (η^1 -eox) (yellow) | or P2 ₁ ,2 ₁ 8 | 7.003(1) 16.573(1) 29.088(4) | | PtC ₂ Cl ₂ N | η^2 C Cl η^1 N | 2.165(20,5) 2.282(6,1) 2.10(1) | Cl,Cl Cl,N | 177.6(2) 88.9(4,1.7) | [63] |
| | | | | PtC ₂ Cl ₂ N | η^2 C Cl η^1 N | 2.18(2,3) 2.288(6,1) 2.10(1) | Cl,Cl Cl,N | 177.3(2) 88.8(4,2.5) | |

(Table 2).contd.....

| | | | | | | | | | |
|---|------------------------------|--------------------------------------|----------------------------------|--|---|--|--|---|------|
| Pt(η^4 -cod)(η^2 -metu) (pale yellow) (at 130 K) | m P2 ₁ /c 8 | 11.270(3) 12.268(2) 17.053(4) | 96.00(2) | PtC ₄ NS | η^4 C η^2 N η^2 S | 2.16(1,1) 2.20(1,1) 2.00(1) 2.318(3) | C,C N,S C,N C,S | 82.0(5,6) 70.7(3) ^e 99.6(5,4) 156.3(4) 101.6(3,1.6) | [64] |
| | | | | PtC ₄ NS | η^4 C η^2 N η^2 S | 2.17(1,0) 2.19(1,1) 2.01(1) 2.303(3) | C,C N,S C,N C,S | 81.4(5,1) 70.7(3) ^e 100.8(4,1.1) 155.7(5) 100.9(3,2.1) | |
| [Pt(η^2 -dmphen)(η^2 -PhC≡CPh)I ₂].CHCl ₃ (dark red) | or Cmc ₂₁ 8 | 14.367(3) 15.529(3) 26.959(5) | | PtN ₂ C ₂ I ₂ | η^2 N η^2 C I | 2.28(2,0) 2.01(2,0) 2.647(3,22) | N,N C,C I,I N,C N,I C,I | 71.9(6) ^e 36.1(8) 178.7(1) 125.7(7) 89.5(5,3,2) 90.6(6,2,8) | [65] |
| | | | | PtN ₂ C ₂ I ₂ | η^2 N η^2 C I | 2.22(2,0) 2.08(3,0) 2.644(3,28) | N,N C,C I,I N,C N,I C,I | 74.9(7) ^e 35.5(10) ^e 179.5(1) 124.8(9) 90.2(5,4) 89.8(7,2) | |
| [Pt ^{IV} (η^2 -bpy)(η^2 -mq). (Me) ₂ BF ₄ ·0.75CH ₂ Cl ₂] (white) | m C2/c 16 | 40.624(4) 12.890(1) 19.765(2) | 91.347(2) | PtN ₃ C ₃ | η^2 N η^2 N η^2 C MeC | 2.15(1,1) 2.151(9) 2.05(1) 2.05(1,2) | N,N C,C N,C | 76.1(4) ^e 89.4(6,2,0) 82.6(5) ^e 96.8(5) 172.8(5,2) | [66] |
| | | | | PtN ₃ C ₃ | η^2 N η^2 N η^2 C MeC | 2.13(1,2) 2.17(1) 2.04(1) 2.04(2) 2.07(1) | N,N C,C N,C | 77.3(4) ^e 89.9(6,3,8) 82.0(5) ^e 97.9(5) 174.8(5,4) | |
| [Pt ^{IV} (η^3 -htpzb)(Ph) ₂ I] ₂ (I) ₃ (black) | tr P-1 4 | 18.614(4) 13.114(9) 11.794(11) | 78.14(7) 86.69(7) 88.24(4) | PtN ₃ C ₂ I | η^3 N PhC I | 2.01(2) 2.15(2) 2.20(2) 2.07(3,2) 2.601(3) | N,N C,C N,C N,I C,I | 84.5(9,6) ^e 98(1) 89(1,1) 177(1,0) 91.4(6,6) 174.8(5) 93.9(9,1) | [67] |
| | | | | PtN ₃ C ₂ I | η^3 N PhC I | 2.11(3,1) 2.18(3) 2.03(3) 2.43(3) 2.63(4) | N,N C,C N,C N,I C,I | 82(1,2) ^e 100(2) 93(1,1) 173(1) 96.2(2,4,5) 172.9(8) 95(2,4) | |

(Table 2).contd.....

| | | | | | | | | | |
|---|------------------------------|-------------------------------------|------------------------------------|---|--|---|---------------------------------|--|------|
| Pt ^{IV} (η^1 -CH ₂ Ph)(η^2 -thpy) ₂ Br (pale brown) | tr P-1 4 | 9.854(2) 15.413(2) 17.333(2) | 63.90(1) 76.71(1) 86.42(1) | PtC ₃ N ₂ Br | η^1 C η^2 C η^2 N Br | 2.114(5) 1.998(5,6) 2.156(4,4) 2.5619(7) | C,N | 79.9(2,2) ^e | [68] |
| | | | | PtC ₃ N ₂ Br | η^1 C η^2 C η^2 N Br | 2.114(5) 2.004(5,5) 2.163(4,10) 2.5637(7) | C,N | 80.0(2,2) ^e | |
| Pt ^{IV} (Me) ₃ (η^2 -dmpbp) ₂ I (pale yellow) (at 120(2) K) | tr P-1 4 | 8.954(8) 14.943(6) 15.634(4) | 105.85(2) 96.61(2) 90.90(2) | PtC ₃ N ₂ I | MeC η^2 N I | 2.056(9,9) 2.169(7) 2.254(7) 2.8016(10) | C,C N,N C,N C,I N,I | 89.0(4,5,1) 74.7(3) ^e 96.7(4,8,2) 175.1(4,4,0) 92.4(3,7) 178.6(3) 86.5(2,1,0) | [69] |
| | | | | PtC ₃ N ₂ I | MeC η^2 N I | 2.047(9,10) 2.179(7) 2.270(7) 2.7781(12) | C,C N,N C,N C,I N,I | 86.8(2,3,9) 75.2(3) ^e 96.1(4,7,6) 176.1(4,2,7) 91.6(3,1,1) 178.3(3) 88.3(3) | |
| [Pt ^{IV} (py) ₂ { η^2 -C ₃ H ₄ (Ph) ₂ }Cl ₂]. 0.5EtOH (pale yellow) | tr P-1 4 | 13.148(6) 14.052(7) 17.860(8) | 62.53(1) 108.25(3) 114.69(3) | PtN ₂ C ₂ Cl ₂ | pyN η^2 C Cl | 2.18(4,3) 2.09(5,3) 2.31(1,0) | N,N C,C Cl,Cl | 82(1) 70(2) ^f 177.8(5) | [70] |
| | | | | PtN ₂ C ₂ Cl ₂ | pyN η^2 C Cl | 2.25(3,9) 2.11(3,6) 2.31(1,1) | N,N C,C Cl,Cl | 92(1) 76(1) ^f 176.6(3) | |
| Pt(Me) ₃ (η^2 -C ₃ H ₃ NP ₂)I (white) | or Pca2 ₁ 8 | 27.131(5) 11.779(2) 21.396(4) | | PtC ₃ NPI | MeC η^2 N η^2 P I | 2.04(3,3) 2.13(3) 2.25(2) 2.406(9) 2.853(6) | C,N N,I P,I | 178.6(8) 83.0(5) 91.7(3) | [71] |
| | | | | PtC ₃ NPI | MeC η^2 N η^2 P I | 2.11(3,0) 2.15(3) 2.22(2) 2.359(9) 2.825(6) | C,N N,I P,I | 178.0(8) 83.0(5) 92.3(3) | |
| [Pt(η^4 -bdpb)Cl]Cl ^h | m C2/c 24 | 39.128(8) 17.656(3) 38.513(4) | 118.36(2) | PtC ₃ ClP | η^4 C η^4 P Cl | 2.13(4) 2.19(5,1) 2.34(1) 2.40(1) | C,C C,Cl C,P Cl,P | 37(2) ^f 87(2,3) 86(2,2) 171(1) 95(1) ⁱ 162(1,1) 94(1) | [72] |

(Table 2).contd.....

| | | | | | | | | | |
|---|----------------|------------------------------------|----------------------------------|----------------------|---|--|----------------------------|---|------|
| | | | | PtC ₃ CIP | η^4 C η^4 P Cl | 2.09(3) 2.17(5,2) 2.31(1) 2.40(1) | | not given | |
| | | | | PtC ₃ CIP | η^4 C η^4 P Cl | 2.06(3) 2.22(4,1) 2.32(1) 2.41(1) | | not given | |
| [Pt(η^2 -dmaen)(η^2 -msedpa)]. ClO ₄ ^{-j} (colorless) | tr P-1 4 | 7.950(2) 17.449(3) 21.981(4) | 82.67(2) 87.06(2) 82.87(2) | PtNCSAs | η^2 N η^2 C η^2 S η^2 As | 2.139(11) 1.987(13) 2.329(4) 2.359(1) | N,C N,S C,As S,As | 86.3(5) ^e 99.3(3) 96.4(4) 84.8(1) ^e | [73] |
| | | | | PtNCSAs | η^2 N η^2 C η^2 S η^2 As | 2.110(12) 1.983(15) 2.311(4) 2.336(2) | N,C N,S C,As S,As | 81.7(5) ^e 96.3(3) 96.6(4) 85.1(10) ^e | |
| | | | | PtNCSAs | η^2 N η^2 C η^2 S η^2 As | 2.129(11) 2.064(13) 2.316(4) 2.345(2) | N,C N,S C,As S,As | 80.3(5) ^e 94.9(3) 98.1(4) 86.6(1) ^e | |
| | | | | PtNCSAs | η^2 N η^2 C η^2 S η^2 As | 2.114(10) 2.071(13) 2.336(5) 2.351(2) | N,C N,S C,As S,As | 79.5(5) ^e 97.5(3) 97.5(3) 85.7(1) ^e | |

Footnotes: a.) Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b.) The chemical identity of the coordinated atom or ligand is specified in these columns.

c.) Three - membered metallocyclic ring.

d.) Mean values for both molecules are given in original paper.

e.) Five-membered metallocyclic ring.

f.) Six - membered metallocyclic ring.

g.) Four - membered metallocyclic ring.

h.) Three crystallographically independent molecules.

i.) Nine - membered metallocyclic ring.

j.) Four crystallographically independent molecules.

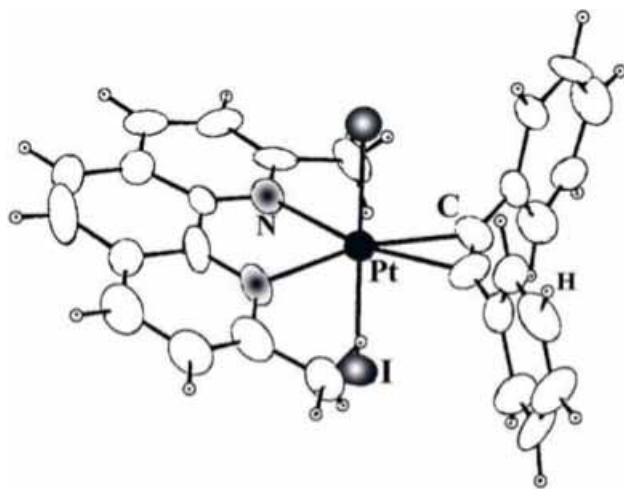


Fig. (2). Structure of one isomeric form of [Pt(η^2 -PhC≡CPh)(η^2 -dmphen)I₂].CHCl₃ [65].

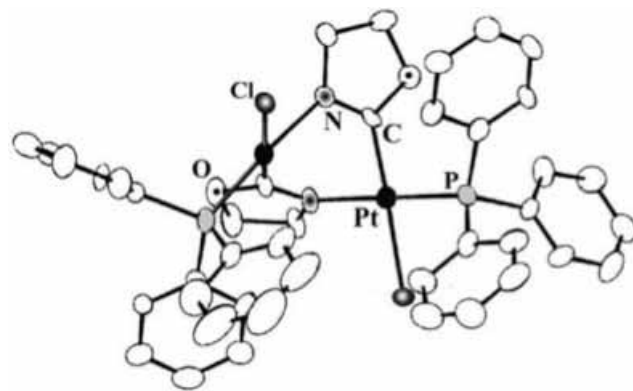


Fig. (3). Structure of one independent molecule of [Pt(μ - η^2 -COCH₂CH₂N)(Cl)(PPh₃)₂] [79].

In yellow Pt₂(Me)₆(μ -salal)₂ [77] dimerisation occurs by formation of a four - membered centrosymmetrical Pt(O)₂Pt ring *via* the phenolic oxygen. Around each Pt(IV) atom there

(Table 3).contd.....

| | | | | | | | | | | |
|---|------------------------------|-------------------------------------|-----------------------------------|---------------------------------|---|---|--------------------------|---|--|------|
| | | | | PtN ₂ CP | μN MeC Ph ₃ P | 2.14(1,0) 2.08(1) 2.204(2) | 3.117(1) N 95.1(3) | N,N C,P N,C N,P | 78.2(3) 88.9(3) 90.3(4) 168.5(3) 102.5(2) | |
| [Pt(μ-η ² -COCH ₂ CH ₂ N). (Cl)(PPh ₃) ₂] ₂ . 0.5ClCH ₂ CH ₂ Cl (yellow) | tr P-1 4 | 19.564(3) 16.497(3) 13.243(2) | 88.93(3) 97.88(3) 91.97(3) | PtNCCIP | μη ² N μη ² C Cl Ph ₃ P | 2.07(2,0) 1.95(2,2) 2.452(4,11) 2.239(6,6) | 3.407(1) | N,C Cl,P N,Cl N,P C,Cl C,P | 85.8(7,1) 91.2(2,3) 91.0(2,5) 174.8(5,3) 174.5(6,1.4) 93.7(6,8) | [79] |
| | | | | PtNCCIP | μη ² N μη ² C Cl Ph ₃ P | 2.05(1,1) 1.97(2,2) 2.450(4,3) 2.236(6,7) | 3.420(1) | N,C Cl,P N,Cl N,P C,Cl C,P | 84.2(7,2) 93.8(2,9) 89.2(3,2) 172.1(4,2) 171.4(5,9) 93.4(6,4) | |
| Pt ₂ (μ-η ² -dmpm) ₂ (Me) ₄ (colourless) | m P2 ₁ /a 4 | 16.634(4) 11.112(3) 12.469(3) | 103.40(2) | PtC ₂ P ₂ | μη ² P MeC | 2.270(4,6) 2.168(12,13) | 4.198(1) | P,P C,C P,C | 102.7(2) 82.8(5) 87.5(4,2) 169.7(4,2) | [80] |
| | | | | PtC ₂ P ₂ | μη ² P MeC | 2.280(3,0) 2.142(12,18) | 4.276(1) | P,P C,C P,C | 102.9(2) 83.4(5) 86.9(4,4) 170.3(4,3) | |
| [Pt ₂ (μ-H)(Ph) ₂ (Pme ₃) ₄]. Bph ₄ (white) | tr P-1 4 | 13.731(5) 16.192(2) 23.425(8) | 96.46(2) 100.54(3) 95.05(2) | PtP ₂ HC | μH Me ₃ P PhC | 1.76(8,3) 2.288(4,6) 2.306(4,4) 2.05(3,1) | 3.061(7) H 121(5) | P,P P,C | 170.2(1,2) 87.3(4,2.2) 166.0(4,1.7) | [81] |
| | | | | PtP ₂ HC | μH Me ₃ P PhC | not given 2.286(4,5) 2.04(4,2) | 3.0969(9) H not given | P,P P,C | 172.0(2,4) 87.2(4,6) 166.0(5,1.0) | |
| Pt ₂ (μ-η:η-btmset). (Pet ₃) ₄ (Ph) ₂ (pale yellow) | tr P-1 3 | 16.804(3) 25.107(5) 9.221(2) | 98.40(3) 99.67(3) 88.12(3) | PtC ₂ P ₂ | μηC PhC Et ₃ P | 2.03(2,1) 2.09(1,1) 2.286(6,12) | | C,C P,P C,P | 176(2,2) 176.4(2,7) 89.1(6,2.4) | [82] |
| | | | | PtC ₂ P ₂ | μηC PhC Et ₃ P | 2.03(2) 2.09(2) 2.2985,5) | | C,C P,P C,P | 179.0(7) 176.1(2) 89.3(5,2.1) | |
| Pt ₂ (μ-η:η-btmsebt). (Pet ₃) ₄ (Ph) ₂ (yellow) | tr P-1 2 | 15.870(6) 17.460(8) 9.525(4) | 97.28(3) 90.80(3) 82.06(3) | PtC ₂ P ₂ | μηC PhC Et ₃ P | 1.96(2) 2.03(2) 2.312(6,5) | | C,C P,P C,P | 179.0(8) 178.2(2) 90.2(6,2) | [82] |
| | | | | PtC ₂ P ₂ | μηC PhC Et ₃ P | 2.05(2) 2.06(2) 2.293(6,3) | | C,C P,P C,P | 176.8(7) 174.5(2) 89.9(5,2.4) | |

(Table 3).contd.....

| | | | | | | | | | | |
|--|------------------------------|--|--------------------------------------|--|---|--|---|--------------------------|--|------|
| [Pt ₂ (μ-η:η-C ₁₇ H ₈)(PEt ₃) ₄ . (Ph) ₂].0.33C ₆ H ₁₄ (colourless) | tr P-1 3 | 9.220(1) 19.960(1) 22.910(2) | 102.76(2) 93.83(2) 93.69(2) | PtC ₂ P ₂ | μη ² C PhC Et ₃ P | 2.03(2,1) 2.05(2,1) 2.275(5,9) | | P,P C,P | 174.3(2,2.7) 90.3(5,2.8) | [83] |
| | | | | PtC ₂ P ₂ | μη ² C PhC Et ₃ P | 2.01(2) 2.05(2) 2.272(6,5) | | P,P C,P | 175.6(2) 89.9(6,1.0) | |
| B. TRINUCLEAR | | | | | | | | | | |
| [Pt ₃ (μ-CO) ₃ (PBu ^t Ph) ₃]. 0.25thf (red) | tr P-1 4 | 16.096(2) 22.376(3) 13.700(2) | 91.03(1) 92.32(1) 89.38(1) | Pt ⁰ C ₂ P | μOC P | 2.008(20,11) 2.031(19,4) 2.099(16) 2.296(5,6) | 2.672(1,1) 2.677(1) C 82.8(7,2.2) | C,C C,P Pt,Pt | 147.5(7,2) 104.0(5,3.1) 60.0(1,1) | [84] |
| | | | | Pt ⁰ C ₂ P | μOC P | 2.031(18,14) 2.298(4,4) | 2.673(1) 2.683(1,1) C not given | C,C C,P Pt,Pt | 145.7(7,6.1) 104.5(5,3.7) 60.0(1,3) | |
| Pt ₃ (μ-PBu ^t) ₃ (H)(CO) ₂ (orange) | m P2 ₁ /c 8 | 16.596(3) 21.664(6) 19.487(7) | 91.01(1) | Pt ^{II} P ₂ HPT ₂ | μP H | 2.270(3,2) not given | 2.7165(6) 2.7247(6) P 73.56(9,10) | P,P Pt,Pt | 169.6(1) 82.32(2) | [85] |
| | | | | Pt ^I P ₂ C (x2) | μP OC | 2.275(3,1) 2.350(5,16) 1.83(1,1) | 3.6135(6) P 101.3(1) | P,P P,C | 140.7(1,2) 106.9(5,10) 165.4(5,9) | |
| | | | | Pt ^{II} P ₂ HPT ₂ | μP H | 2.275(3,2) not given | 2.7196(6) 2.7246(6) P 73.46(9,3) | P,P Pt,Pt | 169.8(1) 83.49(2) | |
| | | | | Pt ^I P ₂ C (x2) | μP OC | 2.277(3,5) 2.341(3,10) 1.84(2,3) | 3.6249(6) P 102.0(1) | P,P P,C | 140.5(1,2) 108.2(4,2) 164.4(4,4) | |
| Pt ₃ (μ-dmaet)(μ-η:η- dmaet)(Me) ₆ (yellow) | m P2 ₁ /c 8 | 16.598(4) 8.751(2) 46.360(11) | 92.18(6) | Pt ^{II} S ₄ | μS | 2.319(9,0) 2.331(9,4) | S 94.5(3,1.0) | S,S | 90.1(3,8.8) 174.3(3,1.8) | [86] |
| | | | | Pt ^{IV} C ₃ S ₂ N (x2) | μS N MeC | 2.480(9,4) 2.420(9,11) 2.29(3,2) 2.08(4,2) | | C,C S,S C,S S,N | 88(2,2) 79.4(3,6) 93.8(4,5.3) 175.7(3,2.3) 85.2(8,7) ^c | |
| | | | | Pt ^{II} S ₄ | μS | 2.321(9,1) 2.327(9,8) | S 95.2(3,1.6) | S,S | 90.0(3,7.5) 177.6(3,3) | |
| | | | | Pt ^{IV} C ₃ S ₂ N (x2) | μS N MeC | 2.470(9) 2.429(9) 2.25(3,3) 2.05(5,6) | | C,C S,S C,S S,N | 89(2,6) 79.6(3,1) 93.2(5,7.5) 176.4(5,1.7) 85.9(10,5) ^c | |
| C. TETRANUCLEAR | | | | | | | | | | |
| Pt ₄ (μ-CO) ₃ (PEt ₃) ₄ (dark gray) | tr P-1 4 | 11.364(15) 19.954(19) 19.832(30) | 103.96(10) 104.24(11) 91.52(9) | Pt ⁰ C ₃ P (x2) | μOC Et ₃ P | 2.00(-,5) 2.268(-,11) | 2.691-2.766 3.190 C 83.6(-,5.5) | | not given | [87] |

(Table 3).contd.....

| | | | | | | | | | | |
|---|----------------|---------------------------------|--------------------------------|--|--------------------------|--|---|-------------------|---|------|
| | | | | Pt ⁰ C ₂ P (x2) | μOC Et ₃ P | 2.06(-,2) 2.24 2.228(-,6) | | | | |
| | | | | Pt ⁰ C ₃ P (x2) | μOC Et ₃ P | 2.06(-,6) 2.20(-,6) 2.257(-,1) | 2.704-2.745 3.263 C 83.6(-,2,4) | | not given | |
| | | | | Pt ⁰ C ₂ P (x2) | μOC Et ₃ P | 1.85(-,3) 2.02 2.239(-,26) | | | | |
| [Pt ₄ (μ ₃ -I) ₄ (Me ₁₂).0.5MeI (colourless)] | rh R3 12 | 10.3139(4) 90.555(8) | | Pt ^{IV} C ₃ I ₃ (x4) | μ ₃ I | 2.8105(8) 2.8328(8,38) 2.059(13,14) | 4.105(1) I 93.0(1,5) | C,C I,I C,I | 88.4(6,1.0) 86.7(1,4) 92.5(4,3.0) 177.5(4,1.1) | [88] |
| | | | | Pt ^{IV} C ₃ I ₃ (x4) | μ ₃ I MeC | 2.8229(8,44) 2.8316(8,14) 2.059(13,20) | 4.105(1) I 93.0(1,2) | C,C I,I C,I | 88.5(6,1.0) 86.7(1,4) 92.8(4,3.0) 176.7(4,7) | |
| Pt ₄ (μ-Cl) ₄ (μ-η ³ -allyl) ₄ | tr P-1 4 | 13.34(3) 16.16(3) 8.33(1) | 90.2(2) 100.2(2) 93.2(2) | PtC ₃ Cl ₃ (x4) | μCl η ³ C | 2.37(2,1) 2.49(2,3) 1.98(8,11) 2.20(12,7) | 3.236(4,12) 3.278(4,5) Cl 83.7(6,1.2) | Cl,Cl | 85.0(7,7) | [89] |
| | | | | PtC ₃ Cl ₃ (x4) | μCl η ³ C | 2.37(2,3) 2.49(2,2) 2.08(9,5) 2.20(9,5) | 3.233(4,3) 3.262(4,0) Cl 83.6(7,8) | Cl,Cl | 85.0(7,5) | |

Footnotes: a). Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b). The chemical identity of the coordinated atom or ligand is specified in these columns.

c). Five-membered metallocyclic ring.

are three methyl groups in the cis configuration, two oxygen atom forming a chelate salicylaldehyde, and one bridging oxygen atom (PtO₃C₃). The mean Pt – O – Pt bridge angle and Pt...Pt separation are 100(1)° and 3.407(4) Å (molecule 1) and 102(1)° and 3.418(4) Å (molecule 2).

The asymmetric unit of colourless [Pt₂(μ-NH₂)₂(Me)₂(PPh₃)₂] [78] consists of two independent but chemically identical half molecules on sites with a common 2-fold rotation axis. Two {Pt(Me)(PPh₃)}⁺ fragments are connected by two NH₂ groups, which serve as bridges and form a four – membered centrosymmetrical Pt(N)₂Pt ring, with the mean Pt – N – Pt bond angles of 95.2 and 95.1° and Pt(II) ... Pt(II) separations of 3.106(1) and 3.117(1) Å, respectively.

The structure of one of the two independent molecules of yellow [Pt(μ-η²-COCH₂CH₂N)(Cl)(PPh₃)₂] [79] is shown in (Fig. 3). Each dimer is formed by two bridging COCH₂CH₂N ligands which are coordinated by one Pt(II) on one side *via* a Pt – N bond and to the second Pt(II) *via* Pt – C bond forming a six membered (-Pt – C – N -)2 ring. The Pt(II) ...Pt(II) separations are 3.407(1) and 3.420(1) Å. The coordination geometry around each Pt(II) atom is an irregular square with

deviation in the tetrahedral direction of the bonded atoms (PtNCCIP).

Structure of colourless Pt₂(μ-η²-dmpm)₂(Me)₄ [80] contains the eight membered {PtPCP-}₂ ring with Pt(II) ... Pt(II) separations of 4.198(1) Å (molecule 1) and 4.276(1)Å (molecule 2). The ring adopts the twist - sadl conformation. Each Pt(II) atom displays a cis – square – planar coordination (PtC₂P₂).

In white [Pt₂(μ-H)(Ph)₂(PMe₃)₄]BPh₄ [81] both complex cations contain the two planar {Pt(Ph)₂(PMe₃)₂} moieties bridged by a single hydride ligand. The Pt(II) ... Pt(II) distances are 3.061(7) and 3.0969(9) Å. The Pt – H – Pt bridge angle is 121(5)°.

There are two Pt(II) dimers: pale yellow and yellow [82] and both contain two independent dimer molecules. In each case, the crystal structure consists of discrete dimeric molecules. A pair of Pt(Ph)(PEt₃)₂ fragments are bridged by a thiophenediyl or bis- (acetylide) ligand for the pale yellow and yellow, respectively. Each Pt(II) atom has a trans – square – planar geometry (PtC₂P₂).

In colourless [Pt₂(μ-η:η-C₁₇H₈)(PEt₃)₄(Ph)₂]. 0.33 C₆H₁₄ [83] two Pt(Ph)(PEt₃)₂ fragment are bridged by 2,7-

bis(ethynyl) fluorene. Each Pt(II) has a trans-square planar geometry (PtC₂P₂).

There are three trimer derivatives each containing two independent trimeric molecules (Table 3B). In red [Pt₃(μ-CO)₃(PBU₂Ph)₃]. 0.25thf [84] each molecule contains a triangular core of Pt₃ atoms. The angle between the Pt₃ planes in the two different molecules is 95.0°. The Pt – Pt distances span a range 2.672(1) to 2.677(1) Å in one and 2.673(1) to 2.684(1) in another molecule. Each Pt – Pt edge is bridged by CO group and PBU₂Ph ligand is attached to each Pt(0) atom.

The structure of orange Pt₃(μ-PBU₂)₃(H)(CO)₂ [85] contains an “open” triangular Pt₃ units with two short Pt(I) – Pt(II) bond distances and a long Pt(I) ... Pt(I) separation, each side of this unit is symmetrically bridged by a μ-PBU₂ group. The mean Pt(II) – Pt(I) bond distances and Pt(I) ... Pt(I) separations are 2.721 and 3.613 Å (molecule 1) and 2.722 and 3.625 Å (molecule 2). The Pt(I) – P – Pt(II) and Pt(I) – Pt – P(1) bridge angles are 73.6 (av.) and 101.3(1)° (molecule 1) and 73.5 (av.) and 102.0(1)° (molecule 2), respectively. In this mixed-valence triplatinum (I, I, II), each Pt(I) atom has tetrahedral (PtP₂CPt(II)) and Pt(II) square-planar (PtP₂Pt₂(I)) arrangement.

The structure of one of two independent molecules of [Pt₃(dmaet)₄(Me)₆] [86] is shown in (Fig. 4). As can be seen, two Pt(IV) (Me)₃(SCH₂CH₂NMe₂)₂ moieties are connected through the pairs of S donor atoms which coordinated to the central Pt(II) atom. Each Pt(IV) atom shows distorted pseudo octahedral geometry (PtC₃S₂N). The Pt(II) atom in each molecule shows distorted square planar geometry (PtS₄) (Table 3B).

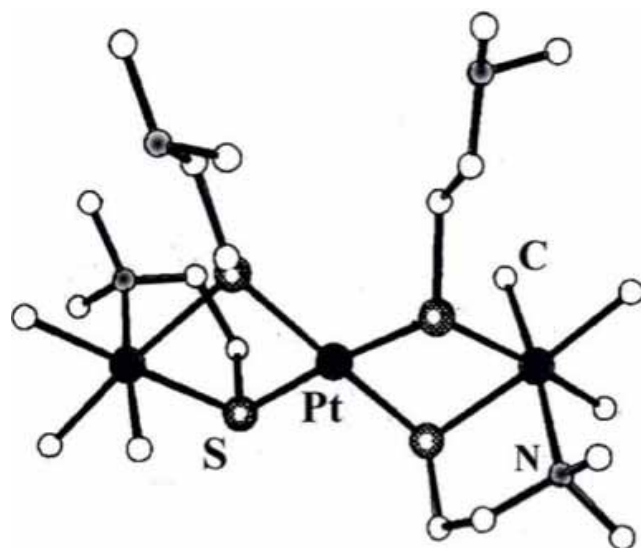


Fig. (4). Structure of one independent molecule of [Pt₃(dmaet)₄(Me)₆] [86].

There are also three tetranuclear derivatives, which contain two crystallographically independent molecules, as well (Table 3C). In each molecule of dark gray Pt₄(μ-CO)₅(PEt₃)₄ [87], the four Pt(0) atoms are located at the apices of a deformed tetrahedron (butterfly), in which five edges have Pt-Pt bond lengths in range 2.69-2.766 (av. 2.731 Å) and 2.704-2.745 (av. 2.727 Å) (in molecule 1 and 2) respectively while the six edge, are extended to 3.190 and 3.263 Å, respec-

tively. Bridging CO groups are bound to each shortened edge of Pt₄ tetrahedron. The PEt₃ molecules are terminal ligands of the Pt(0) atom.

The structure of colourless [Pt₄(μ³-I)₄(Me)₁₂]. 0.5MeI [88] is shown in (Fig. 5). Each cluster has C₃ symmetry. A distorted “cubane skeleton” was found for the cluster, with octahedrally coordinated Pt(IV) atom (PtC₃I₃) and tetrahedrally coordinated iodine atoms. The sum of six Pt – L bond distances in molecule 1 is 15.404 Å which is about 0.036 Å smaller than that found in molecule 2, which means that the former is less crowded than the latter. The mean Pt...Pt separation is 4.105(1) Å and mean Pt – I – Pt bridge angle 93.0°.

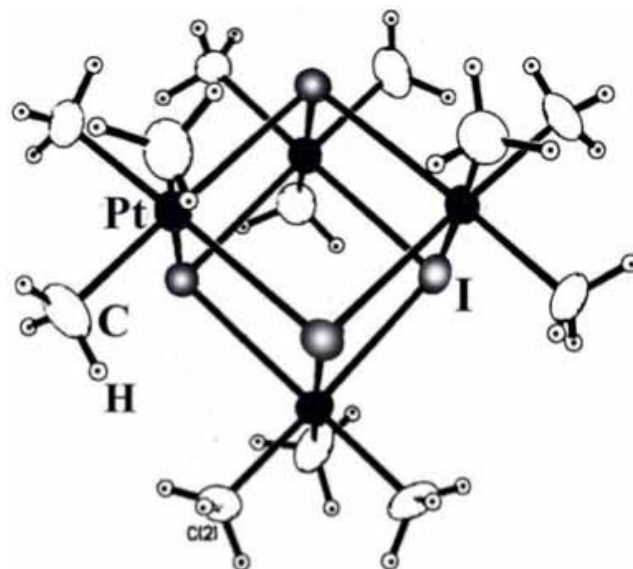


Fig. (5). Structure of one independent molecule of [Pt₄(μ³-I)₄(Me)₁₂].0.5 MeI [88].

Inspection of the data in Tables 1-3 reveals that there are over ninety platinum distortion isomers, which can be divided into several subgroups. In the series of mononuclear derivatives one example, Pt(II)(CH₂Cl)(η₃-tmba)Cl [37] exists in three isomeric forms. Nineteen exist in two isomeric forms (Pt(0) [7], Pt(II) [8-34], Pt(IV) [35, 36]). One example Pt(II)(SMe₂)₂(Ph)(Cl) [12] exists in two isomeric forms (triclinic and monoclinic) and monoclinic contains two crystallographically independent molecules.

There are thirty six examples (Pt(0) [38-42], Pt(II) [12, 37, 42-65], Pt(IV) [66-71]) which contains two crystallographically independent molecules. One example, [Pt(II)(η⁴-bdpb)Cl]Cl [72] contains three such molecules and another one [Pt(II)(η²-dmaen)(η²-msedpa)].ClO₄ [73] contains even four such molecules.

Bi-, tri- and tetranuclear derivatives are found only derivatives, which contain two crystallographically independent molecules. The platinum in these derivatives are found in the oxidation states of zero [84, 87], +1 [74], +2 [75, 76, 79-83, 89], and mixed valence Pt(I)(x2) plus Pt(II) [85] and Pt(II) plus Pt(IV) (x2) [86].

In this series of distortion isomers the Pt(0) atoms are tetrahedrally coordinated (PtP₃C [7, 8], PtC₄ [38], PtC₂P₂ [39-42], PtC₂PPT' [84,87]). The mean Pt(0) – L bond distances elongated in the order: 1.86 Å (CO) < 2.055 Å (μ-CO)

< 2.066 Å (bi-CL) < 2.273 Å (bi-PL) < 2.278 Å (PL). The Pt(0) – Pt(0) bond distances range from 2.671(1) – 2.766(1) Å (av. 2.709 Å).

The Pt(I) is tetrahedrally coordinated (PtCSPPt⁺) [74] with the mean Pt(1) – L bond distances elongated in the order: 1.845 Å (CO) < 2.263 Å (μ-S) < 2.267 Å (μ-PL) <

Table 4. Crystallographic and Structural Data for Platinum Organometallic Complexes – Cis- and Trans- Isomers^a

| COMPOUND (colour) | Cryst. cl. SPACE GR. Z | a[Å] b[Å] c[Å] | α[°] β[°] γ[°] | Chromo- PHORE | Pt – L [Å] | | L – Pt – L [°] | | Ref. |
|--|------------------------------|----------------------|----------------------|---------------------------------|-------------------|--------------|------------------------------|--------------|------|
| | | | | | | | | | |
| cis-[Pt(ozl) ₂ (CN) ₂].H ₂ O (orange) | tr | 8.085(2) | 78.78(1) | PtC ₄ | NC ^b | 1.997(8,7) | C,C ^b | 90.0(3,4,7) | [90] |
| | P-1 | 8.379(2) | 71.17(1) | | ozlC | 2.015(7,5) | | 176.1(3,1.2) | |
| | 2 | 8.669(1) | 79.09(1) | | | | | | |
| trans-[Pt(ozl) ₂ (CN) ₂] (colourless) | m | 8.331(2) | 92.80(2) | PtC ₄ | NC | 1.973(8,0) | C,C | 89.2(3) | [90] |
| | P2 ₁ /n | 7.259(3) | | | ozlC | 2.004(0,0) | | 180.0(3) | |
| | 2 | 9.578(3) | | | | | | | |
| cis-Pt{CH ₂ =C(Me)}. (C≡CBu [†])(PPh ₃) ₂ (colourless) | m | 14.000(3) | 90.50(1) | PtC ₂ P ₂ | C | 2.05(2) | C,C P,P C,P | 84.3(7) | [91] |
| | P ₂ /n | 11.991(4) | | | 1.97(2) | 100.3(1) | | | |
| | 4 | 22.602(4) | | | P | 2.340(4) | | 87.7(5,4,6) | |
| | | | | | 2.286(4) | 171.9(4,4,7) | | | |
| trans-Pt{CH ₂ =C(Me)}. (C≡CBu [†])(PPh ₃) ₂ (colourless) | m | 12.724(6) | 97.91(3) | PtC ₂ P ₂ | C | 2.10(1) | C,C P,P C,P | 173.0(5) | [91] |
| | P ₂ /n | 16.762(5) | | | 2.04(1) | 174.5(1) | | | |
| | 4 | 18.779(4) | | | P | 2.295(3,2) | | 90.0(4,4,1) | |
| | | | | | | | | | |
| cis-[Pt(COEt)(COPh)(PPh ₃) ₂]. 0.5C ₆ H ₆ (white) | m | 17.770(8) | 111.52(4) | PtC ₂ P ₂ | C | 2.00(2) | C,C P,P C,P | 81.6(9) | [92] |
| | P2 ₁ /c | 10.537(1) | | | C | 1.98(3) | | 100.5(2) | |
| | 4 | 23.739(9) | | | P | 2.329(6,0) | | 88.9(7,2) | |
| | | | | | | | | 169.0(7,1,1) | |
| trans-[Pt(COEt)(COPh). (PPh ₃) ₂].0.5C ₆ H ₆ (white) | m | 12.204(8) | 102.10(4) | PtC ₂ P ₂ | C | 2.04(2) | C,C P,P C,P | 176.0(8) | [92] |
| | P2 ₁ /n | 14.542(8) | | | C | 2.01(2) | | 175.8(3) | |
| | 4 | 24.659(4) | | | P | 2.306(6,5) | | 90.0(6,3,0) | |
| | | | | | | | | | |
| cis-PtCl ₂ {η-C(PhNCH ₂) ₂ }. (PEt ₃) (colourless) | or Pnam | 15.991(2) | | PtCl ₂ CP | Cl | 2.362(3) | Cl,Cl C,P Cl,C Cl,P | 89.3(1) | [93] |
| | 4 | 8.601(2) | | | ηC | 2.381(3) | | 93.7(4) | |
| | | 16.703(2) | | | Et ₃ P | 2.009(13) | | 91.5(4) | |
| | | | | | | 2.234(3) | | 179.8(4) | |
| | | | | | | | | 86.6(1) | |
| trans-PtCl ₂ {η-C(PhNCH ₂) ₂ }. (PEt ₃) (colourless) | tr | 13.961(6) | 92.98(3) | PtCl ₂ CP | Cl | 2.292(6) | Cl,Cl C,P Cl,C Cl,P | 178.1(2) | [93] |
| | P-1 | 11.782(4) | | | | 2.311(6) | | 177.6(5) | |
| | 2 | 10.659(5) | | | ηC | 2.020(16) | | 89.7(6,1) | |
| | | | | | Et ₃ P | 2.291(4) | | 90.9(2,2,4) | |
| | | | | | | | | | |
| cis-[Pt(PPh ₃) ₂ {η-CH ₂ P(O). (OMe) ₂ }I].H ₂ O (pale yellow) | m | 16.981(3) | 96.71(1) | PtP ₂ CI | Ph ₃ P | 2.257(2) | P,P C,I P,C P,I | 97.97(2) | [94] |
| | P2 ₁ /n | 12.870(3) | | | | 3.331(2) | | 85.4(2) | |
| | 4 | 17.309(3) | | | ηC | 2.124(6) | | 99.8(4) | |
| | | | | | I | 2.6561(7) | | 169.9(2) | |
| | | | | | | | | 85.98(5) | |
| trans-[Pt(PPh ₃) ₂ {η-CH ₂ P(O). (OMe) ₂ }I].Me ₂ CO (pale yellow) | m | 11.678(2) | 107.36(1) | PtP ₂ CI | Ph ₃ P | 2.309(2,4) | P,P C,I P,C P,I | 170.69(8) | [94] |
| | P2 ₁ /n | 19.664(4) | | | ηC | 2.080(8) | | 169.9(2) | |
| | 4 | 18.788(4) | | | I | 2.6774(8) | | 92.4(2,1,0) | |
| | | | | | | | | 88.9(1,1,0) | |

Footnotes: a). Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b). The chemical identity of the coordinated atom or ligand is specified in these columns.

2.277 Å (PPh₃) < 2.346 Å (μ-PL, trans to CO). The Pt(I) – Pt(I) bond lengths are 2.5998(9) and 2.6008(8) Å.

In this series of distortion isomers the predominant square – planar configuration about the Pt(II) atom is cis rather than trans with wide variety of the chromophores and π- complexes, as well. The mean value of Pt(II) – L bond distances (mutually trans) increases in the orders: 2.03 Å (L = C) < 2.07 Å (O or N) < 2.29 Å (P) < 2.30 Å (Cl) < 2.64 Å (I) (monodentate ligands); 2.13 Å (N-unsaturated ligands) < 2.14 Å (C) < 2.25 Å (N-saturated ligands) < 2.26 Å (P) (bidentate ligands). The mean value of Pt(II) – L elongated in the order : 2.02 Å < (uni-) < 2.14 Å (bi- or tri-) < 2.21 Å (tetraordinated). The trans effect on Pt(II) – L bond distances (trans to C), the C donor atom increases the lengths: 2.33 Å (L = P; trans to CO) < 2.38 Å (Cl) < 2.51 Å (Br). The mean value of Pt(II) – L (bridge) bond distance elongated in the order: 1.76 Å (μ- H) < 1.98 Å (μ- CL) < 2.135 Å (μ- NL) < 2.26 Å (μ-PL) < 2.325 Å (μ-SL) < 2.43 Å (μ-Cl).

The Pt(IV) atoms are six coordinated with the chromophores: PtN₂C₂Se₂ [35, 36], PtN₃C₃ [66], PtC₃N₂X (X = I [67, 69] or Br [68]), PtN₂C₂Cl₂ [70], PtC₃NPI [71], PtO₃C₃ [77], PtC₃S₂N [86] and PtC₃I₃ [88].

The mean value of Pt(IV) – L bond length (mutually trans) increases in the orders: 2.07 Å (L=C) < 2.31 Å (Cl) < 2.49 Å (Se) < 2.615 Å (I); 2.11 Å (bi-CL) < 2.15 Å (bi-N unsaturated) < 2.26 Å (bi-N-saturated). The mean value of Pt(IV) – L bond lengths trans to C donor atom ligands (Me, Ph) elongated in the order 2.56 Å (Br) < 2.81 Å (I).

The mean Pt – bonds lengths for the homobidentate ligands, which includes N-, C-, S-, and P- donors, are somewhat shorter than those of the corresponding monodentate ligands except for the P – donor ligands in which the opposite is seen. There is a variety of hetero – bidentate ligands: N/C, N/S, N/P, N/I, C/P, S/P, and S/As donor atoms. The heterotridentate ligands: with 2N/C, N/2C, N/2S and C/2P donor atoms, and tetradentate with 3C/P donor atoms. All of these have mean Pt – L bond distances that follow the same trend as the homobidentate ligands. Correspondingly there is a wide variety of metallocyclic rings, and the effect of both

steric and electronic factors appear in the variation of the internal L – Pt – L angles of metallocyclic rings. The mean chelate rings (L – Pt – L) open in the order: 37.7° (-CC-) < 67.8° (-CCP-) < 69° (-NCC-) < 70.7° (-NCS-) < 73° (-CCC-) < 76° (-NC₂N-, unsaturated) < 80.2° (NC₂C-) < 81.5° (NC₂N-, saturated) < 82.3° (-CC₂P-) < 83.5° (-NC₂I-) < 85.5° (-NC₂S-, and -SC₂As-) < 87° (-PC₂P-).

The mean Pt – Pt distances found in this series of distortion isomers, elongated in the order: 2.600 Å (Pt(I) – Pt(I)) < 2.709 Å (Pt(0) – Pt(0)) < 2.721 Å (Pt(I) – Pt(II)) < 2.756 Å (Pt(II) – Pt(II)).

3. CIS - TRANS ISOMERISM

In the series of platinum organometallic compounds, only five derivatives and all of the monomeric Pt(II) have been found. Their structural parameters are available in Table 4. Structures of cis – and trans- Pt(H₂C=CMe)(C≡CBu^t)(PPh₃)₂ [91] are shown in (Fig. 6) as an example. In three derivatives both isomeric forms belong to the homo-monoclinic [Pt(H₂C=CMe)(C≡CBu^t)(PPh₃)₂ [91], [Pt(COEt)(COPh)(PPh₃)₂].0.5C₆H₆ [92] and [Pt(PPh₃)₂{η-CH₂P(O)(OMe)₂I}.H₂O [94]. In remaining examples differ from each other not only by configuration but also by crystal class. In [Pt(ozl)₂(CN)₂].H₂O [90] cis-isomer is triclinic and trans-monoclinic, and in [PtCl₂{η-C(PhNCH₂)₂}(PEt₃)] [93] cis- is orthorhombic and trans- triclinic.

A square-planar geometry about each Pt(II) atom is created only by unidentate ligands with the chromophores being: PtC₄ [90] PtC₂P₂ [91, 92], PtCl₂CP [93] and PtC₂Cl [94]. The mean values of Pt(II) – L bond distances (mutually trans) elongated in the order: 1.973 Å (CN) < 2.024 Å (CL) < 2.302 Å (Cl) < 2.303 Å (PPh₃). The trans effect on Pt(II) – L bond distances can be divided into two categories. The first in which a hetero-donor atom shortens the trans Pt(II) – L bond and the second in which the trans donor atom elongates the trans length. As an example are Pt(II) – P(PPh₃) bond distances: 2.257 Å (trans to I) < 2.286 Å (trans to CH₂=CMe) < 2.303 Å (mutually trans) < 2.329 Å (trans to COX) < 2.340 Å (trans to C≡CBu^t). (Table 4). Noteworthy, the cis- L-Pt-L bond angles in the cis-isomers are in the

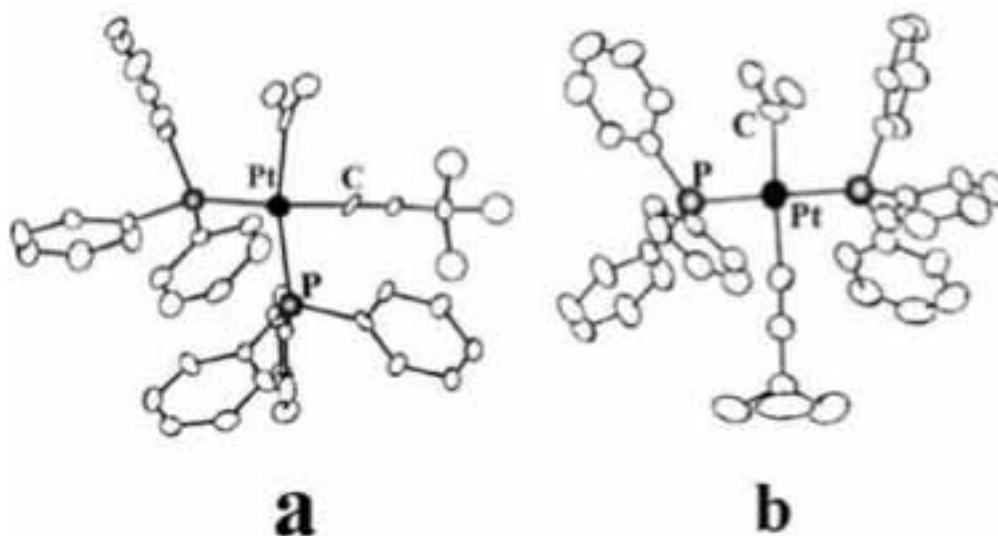


Fig. (6). Structures of Pt(CH₂=CMe)(C≡CBu^t)(PPh₃)₂, cis- (a) and trans- (b) [91].

range 81.6(9) – 100.5(2)°, which is more wide range than that one found in the trans isomer 87.0(2) – 93.0(2)°. The deviation of the trans- L-Pt-L bond angles, in cis- derivatives of 11.6° is somewhat larger than in the trans derivatives of 10° (range 170 – 180°). This indicates that there are somewhat larger distortions in the cis- isomers than in the trans-isomers.

4. LIGAND ISOMERISM

There are three Pt(II) complexes (Table 5) which exhibit this type of isomerism: red orange Pt(η^2 -th-4,5-ppy)₂ and Pt(η^2 -th-5,6-ppy)₂ [95]; yellow PtCl₃(η^2 -C₄H₁₀N-2) [24] and PtCl₃(η^2 -C₄H₁₀N-3) [96]; three yellow PtCl₃(η^2 -C₅H₁₂N-4) [25], PtCl₃(η^2 -C₅H₁₂N-2) [26] and PtCl₃(η^2 -C₅H₁₂N-3) [97]. Structures of Pt(η^2 -th-4,5-ppy)₂ and Pt(η^2 -th-5,6-ppy)₂ [95] are shown in (Fig. 7). The structures of both complexes are very similar. The Pt(η^2 -th-5,6-ppy)₂ (Fig. 7b) has a more distorted structure caused by a stronger steric interaction of the pimeene fragments. This distortion was quantified by considering the Pt – N and Pt – C distances as vectors and

projecting them into the yz plane. In Pt(η^2 -th-4,5-ppy)₂ complex, the (C3' – Pt – C 23') yz and (N 1 – Pt – N 21) yz angles are 13.3 and 11.4°, respectively, whereas the same angles for Pt(η^2 -th-5,6-ppy)₂ are 22.5 and 18.3°. In both complexes the pair of heterobidentate th-4,5 ppy (in orthorhombic) and th-5,6-ppy (in hexagonal) ligands (N, C donors with two five five-membered rings create a square-planar geometry about the Pt(II) atom (PtN₂C₂) with differing degrees of distortion. The mean Pt – N and Pt – C bond distances are 2.157 and 1.992 Å (in orthorhombic complex); 2.170 and 1.947 Å (in hexagonal complex).

There are two monoclinic PtCl₃(η^2 -C₄H₁₀N-n) (n = 2 [24], and 3 [96]) complexes, and three monoclinic PtCl₃(η^2 -C₅H₁₂N-n) (n = 4 [25], 2 [26], and 3 [97]) which are π -complexes. Their structures consist of discrete square – planar molecules in which the Pt(II) atom, the three chlorine atoms and the midpoint of the olefine double bond forms a plane with the platinum at the center. The mean value of Pt(II) – MP (midpoint of the double bond) is 2.05 Å. The mean value of Pt(II) – Cl bond distance (mutually trans) of 2.307 Å is about 0.023 Å shorter than that of the Pt(II) – Cl (trans to

Table 5. Crystallographic and Structural Data for Platinum Organometallic Complexes – Ligand Isomers^a

| COMPOUND (colour) | Cryst. cl. SPACE GR. Z | a[Å] b[Å] c[Å] | | | α [°] β [°] γ [°] | Chromo- PHORE | Pt – L [Å] | | L – Pt – L [°] | | REF. |
|--|---|-------------------------------------|-----------|-------------------|---|----------------------------------|---------------------------------------|--|---|------|------|
| | | Pt – L [Å] | | L – Pt – L [°] | | | | | | | |
| [Pt(η^2 -th-4,5-ppy) ₂]CH ₂ Cl ₂ (red orange) | or P2 ₁ 2 ₁ 4 | 12.973(1) 13.619(2) 17.665(2) | | | | PtN ₂ C ₂ | η^2 N ^b η^2 C | 2.157(7,10) 1.992(10,8) | N,C ^b 80.1(4,1) ^c | [95] | |
| Pt(η^2 -th-5,6-ppy) ₂ (red orange) | hx P6 ₁ 6 | 11.5465(4) 35.356(3) | | | | PtN ₂ C ₂ | η^2 N η^2 C | 2.170(13,4) 1.947(17,29) | N,C 79.0(6,1) | [95] | |
| PtCl ₃ (η^2 -C ₄ H ₁₀ N-2) (yellow) | m P2 ₁ /c 4 | 7.2254(4) 7.521(1) 16.596(1) | 97.77(2) | | | PtCl ₃ C ₂ | Cl η^2 C | 2.297(6,4) 2.320(6) 2.165(20,15) | Cl,Cl 177.5(2) C,C 37.8(10) ^d | [24] | |
| PtCl ₃ (η^2 -C ₄ H ₁₀ N-3) (yellow) | m P2 ₁ /n 4 | 7.953(5) 11.254(6) 10.722(6) | 111.07(4) | | | PtCl ₃ C ₂ | Cl η^2 C | 2.303(6,5) 2.332(6) 2.157(21,20) | Cl,Cl 177.3(2) C,C 38.0(6) ^d | [96] | |
| PtCl ₃ (η^2 -C ₅ H ₁₂ N-4) (yellow) | m P2 ₁ /c 4 | 6.435(5) 9.372(11) 16.737(13) | 100.6(1) | | | PtCl ₃ C ₂ | Cl η^2 C | 2.321(9,0) 2.335(9) 2.182(30,12) | Cl,Cl 177.5(3) C,C 37.6(10) ^d | [25] | |
| PtCl ₃ (η^2 -C ₅ H ₁₂ N-2) (yellow) | m P2 ₁ /c 4 | 11.215(3) 8.729(2) 10.259(3) | 90.0(1) | | | PtCl ₃ C ₂ | Cl η^2 C | 2.314(5,2) 2.321(4) 2.097(14) 2.183(14) | Cl,Cl 174.5(1) C,C 38.1(5) ^d | [26] | |
| PtCl ₃ (η^2 -C ₅ H ₁₂ N-3) (yellow) | m P2 ₁ /c 4 | 8.521(5) 7.569(8) 15.073(16) | 102.45(7) | | | PtCl ₃ C ₂ | Cl η^2 C | 2.302(2,5) 2.341(2) 2.179(11,6) | Cl,Cl 176.1(1) C,C 37.5(4) ^d | [97] | |

Footnotes: a). Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b). The chemical identity of the coordinated atom or ligand is specified in these columns.

c). Five-membered metallocyclic ring.

d). Three – membered metallocyclic ring.

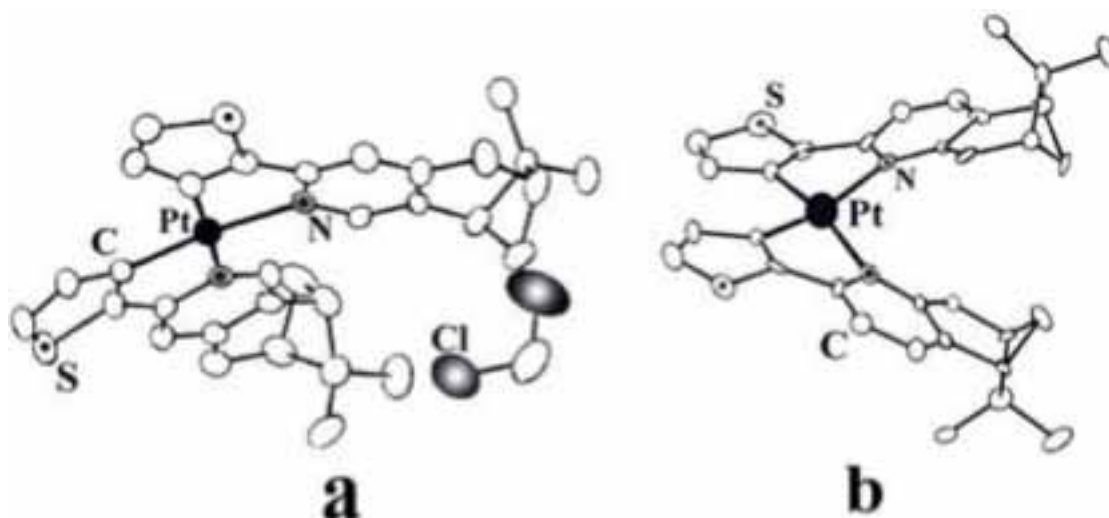


Fig. (7). Structures of $\text{Pt}(\eta^2\text{-th } 4,5 \text{ ppy})_2$ (a) and $\text{Pt}(\eta^2\text{-th } 5,6 \text{ ppy})_2$ (b) [95].

double bond) (2.330 \AA) clearly indicates the trans effect of the olefine double bond.

5. CONCLUSIONS

An analysis of almost one thousand organometallic platinum complexes shows that about 9 % of them exist in isomeric forms. In general the isomers can be subdivided into two major classes, structural and stereochemical. For platinum chemistry, the latter is more prevalent. The stereoisomers found in this review can be subdivided into, distortion (90 %), cis – trans (6 %) and ligand isomers (4 %). Despite the importance of cis – trans geometry in the chemistry of Pt(II) compared to other transition metal systems, within platinum distortion isomerism is far more common. In the series of monomeric Pt coordination compounds where found the following types of isomerism: distortion, cis-trans-, mixed and ligand, from which the distortion is by far prevails (65%) [5].

Distortion isomers, differing only by degree of distortion in Pt – L bond distances and L – Pt – L angles are the most numerous. They are spread over a wider range of oxidation states of platinum, (zero, +1, +2, +4, mixed valence +1 plus +2 and +2 plus +4), from which +2 is the most common. In general, in the series of distortion isomers a variations of Pt – L bond distances as well as of L – Pt – L bond angles, is depend on several factors, oxidation state of Pt (Pt(II) is more favorable), soft donor atoms, (SL, PL, CL, CR and H) are most favorable, crystal packing, etc. In the series of cis-trans and ligand isomers of platinum is found only in oxidation state +2.

The platinum atoms Pt(0) and Pt(I) have a tetrahedral arrangement, most Pt(II) atoms have a square planar (π -complexes included) but some have a trigonal bipyramidal environment, and Pt(IV) atoms are found with octahedral coordination. The coordination about the platinum atom, and correlation between donor atom, bond length and interbond angles with attention to any trans effect, were noted and discussed within each section.

This review with its precursor [5] represents the first overview of the structural data of stereochemistry of plati-

num complexes. Similar review of stereochemistry of heterometallic platinum clusters is in progress.

ACKNOWLEDGMENTS

The authors thank the Ministry of Education of the Slovak Republic, APVT-20-005504 and VEGA 1/2452/05 for financial support.

ABBREVIATIONS

| | | |
|---|---|--|
| bdpep | = | ((2-(benzylthio)phenyl)azophenyl |
| 2 bchp | = | terc-buthylcyclohexylprop-2-yn-1-ol |
| 3 bcn | = | bicyclo[4,2,1]non-1(8)-ene |
| bdpb | = | 1,4-bis[di(terc-butyl)phosphino]butane |
| bpy | = | 2,2'-bipyridyl |
| btmsebt | = | 2,5-bis(trimethylsilylethynyl)bisthiophenediyl |
| btmset | = | 2,5-bis(trimethylsilylethynyl)thiophenediyl |
| Bu ^t | = | terc-butyl |
| bubpy | = | 6-terc-butyl-1,2,2'-bipyridinate |
| chiraphos | = | $\text{Ph}_2\text{PCH}(\text{Me})\text{CH}(\text{Me})\text{PPh}_2$ |
| $\text{C}_4\text{H}_8\text{O}_2$ | = | 1,4-dioxane |
| $\text{C}_4\text{H}_{10}\text{N-2}$ | = | but-2-enylammonium |
| $\text{C}_4\text{H}_{10}\text{N-3}$ | = | but-3-enylammonium |
| $\text{C}_4\text{H}_{12}\text{N}_2$ | = | but-2-en-1,4-diammonium |
| $\text{C}_5\text{H}_{11}\text{NMe}$ | = | N-methyl-4-pentenylammonium |
| $\text{C}_5\text{H}_{12}\text{N}$ | = | pent-X-enylammonium (X = 2, 3 or 4) |
| C_6F_5 | = | pentafluorophenyl |
| $\text{C}_{10}\text{H}_{14}$ | = | tricyclo[3,3,2.0 ^{3,7}]dec-3(7)-ene |
| C_{17}H_8 | = | 2,7-bis(ethynyl)fluorene |
| $\text{C}_{33}\text{H}_{31}\text{NP}_2$ | = | $(\text{PPh}_2)\text{CH}(\text{PPh}_2)\text{CH}_2\text{NHCH}_2\text{Ph}$ |
| cod | = | cycloocta-1,5-diene |
| ctr | = | (cyclohexyl) $\text{N}=\text{C}(\text{CH}_2)_3\text{C}_6\text{H}_3$ |

| | | | | | |
|-------------------------------|---|---|------------|---|-------------------------------------|
| dbpp | = | 1,3-bis(di-terc-buthylphosphine)propane | pyp | = | pyridinium propylide |
| dmaen | = | 1-[1-(dimethylamino)ethyl]-2-naphtadenyl | pzH | = | pyrazole |
| dmaet | = | SCH ₂ CH ₂ NMe ₂ | rh | = | rhombohedral |
| dmpbpy | = | 6-(3,5-dimethylpyrazol-1-yl)-2,2'-bipyridine | salal | = | salicylaldehyde |
| dmphen | = | 2,9-dimethyl-1,10-phenanthroline | sti | = | stilbene |
| dmpm | = | bis(dimethylphosphino)methane | thf | = | tetrahydrofuran |
| dmps | = | (2,2-dimethyl-4-penten-1-yl)methylsulfonium methylide | th-4,5-ppy | = | 2-(2'-thienyl)4,5-pinenopyridinate |
| dmu | = | 1,3-dimethyluracil | th-5,6-ppy | = | 2-(2'-thienyl)-5,6-pinenopyridinate |
| dph | = | 2,5-diphenyl-1,5-hexadiene | thpy | = | 2-(2'-thienyl)pyridine |
| dpp | = | 2,9-diphenyl-1,10-phenanthroline | tmba | = | 2,2,N,N-tetramethyl-3-buten-1-amine |
| dppe | = | 1,2-bis(diphenylphosphino)ethane | tol | = | toluene |
| Et | = | ethyl | trg | = | trigonal |
| eox | = | ethylloxazolidine | tr | = | triclinic |
| had | = | 4-homadamantyne | | | |
| hfp | = | 1,1,1,3,3,3-hexafluoro-3-propanolate | | | |
| htpzb | = | hydridotris(1-pyrazolyl)borate | | | |
| hxemba | = | 1,5-hexadiene-d-methylbenzylamine | | | |
| ia | = | 2-iodoaniline | | | |
| ipa | = | isopropenylacetylide | | | |
| m | = | monoclinic | | | |
| mbpp | = | C(=CH ₂)CH ₂ NHBU ^t | | | |
| mctu | = | N-methyl-N-cyanothioureate | | | |
| Me | = | methyl | | | |
| mppe | = | 1-methyl(phenyl)phosphino-1,2-diphenylethenyl | | | |
| mq | = | 8-methylquinolyl | | | |
| msedpa | = | [2-(methylsulfinyl)ethyl]diphenylarsine | | | |
| or | = | orthorhombic | | | |
| ozl | = | oxazolidin-2-ylidene | | | |
| PBU ₂ ^t | = | di-terc-butylphosphinate | | | |
| Pcy ₃ | = | tricyclohexylphosphine | | | |
| pea | = | α-phenethylamine | | | |
| Ph | = | phenyl | | | |
| phen | = | 1,10-phenanthroline | | | |
| PMe ₃ | = | trimethylphosphine | | | |
| PMePh ₂ | = | diphenylmethylphosphine | | | |
| Pmor ₃ | = | tris(morpholino)phosphine | | | |
| PPh ₃ | = | triphenylphosphine | | | |
| PPR ₃ ⁱ | = | tri-iso-propylphosphine | | | |
| ppy | = | 2-phenylpyridinate | | | |
| ptpc | = | 5-phenyl-1-thia-5-phosphacyclooctane | | | |
| py | = | pyridine | | | |

REFERENCES

- [1] Holloway C.E.; Melnik M. *ORM I*. manuscript in preparation.
- [2] Holloway C.E.; Melnik M. *ORM II*. manuscript in preparation.
- [3] Holloway C.E.; Melnik M. *ORM III*. manuscript in preparation.
- [4] Holloway C.E.; Melnik M. *ORM IV*. manuscript in preparation.
- [5] Melnik M.; Holloway C.E. *Coord. Chem. Rev.*, **2006**, *250*, 2261.
- [6] Melnik M. *Coord. Chem. Rev.*, **1982**, *47*, 239.
- [7] Albano V.G.; Basso Ricci G.M.; Bellon P.L. *Inorg. Chem.*, **1969**, *8*, 2109.
- [8] Albano V.G.; Bellon P.; Sansoni M. *J. Chem. Soc., A*, **1971**, 2420.
- [9] Dryen N.H.; Puddephatt R.J.; Roy S.; Vittal J.J. *Acta Cryst., Sect. C*, **1994**, *50*, 533.
- [10] Evans J.A.; Everitt G.F.; Kenmitt R.D.W.; Russell D.R. *J. Chem. Soc., Chem. Commun.*, **1973**, 158.
- [11] Cheney A.J.; MacDonald W.S.; Flynn K.O.; Shaw B.L.; Turtle B.L. *J. Chem. Soc., Chem. Commun.*, **1973**, 128.
- [12] Kapoor P.; Kukushkin V. Yu.; Lövquist K.; Oscarsson A. *J. Organomet. Chem.*, **1996**, *517*, 71.
- [13] Pandolfo L.; Paiaro G.; Ganis P.; Valle G.; Traldi P. *Inorg. Chim. Acta*, **1993**, *200*, 39.
- [14] Ganis P.; Paiaro G.; Pandolfo L.; Valle G. *Gazz. Chim. Ital.*, **1990**, *120*, 541.
- [15] Osakada K.; Kim Y.J.; Yamamoto A. *J. Organomet. Chem.*, **1990**, *382*, 303.
- [16] Osakada K.; Kim Y.J.; Tanaka M.; Ishiguro S.; Yamamoto A. *Inorg. Chem.*, **1991**, *30*, 197.
- [17] Gorla F.; Venanzi L.M.; Albinati A. *Organometallics*, **1994**, *13*, 43.
- [18] Pedane C.; Benedetti E. *J. Organomet. Chem.*, **1971**, *31*, 403.
- [19] Fu-Yu Tsai; Ray-Hsi Hsu; Tsang-Miao Huang; Jure-Ting Chen; Gene-Hsiang Lee; Yu Wang *J. Organomet. Chem.*, **1996**, *520*, 85.
- [20] Tsang-Miao Huang; Jure-Ting Chen; Gene-Hsiang Lee; Yu Wang *J. Am. Chem. Soc.*, **1993**, *115*, 1170.
- [21] Calapietro M.; Zambonelli L. *Acta Cryst., Sect. B*, **1971**, *27*, 734.
- [22] Elder R.C.; Pesa F. *Acta Cryst., Sect. B*, **1978**, *34*, 268.
- [23] Spagna R.; Venanzi L.M.; Zambonelli L. *Inorg. Chim. Acta*, **1970**, *4*, 283.
- [24] Spagna R.; Venanzi L.M.; Zambonelli L. *Inorg. Chim. Acta*, **1970**, *4*, 475.
- [25] Spagna R.; Zambonelli L. *Acta Cryst., Sect. B*, **1972**, *28*, 2760.
- [26] Spagna R.; Ughetto G.; Zambonelli L. *Acta Cryst., Sect. B*, **1976**, *32*, 2532.
- [27] Mura P.; Spagna R.; Ughetto G.; Zambonelli L. *J. Cryst. Mol. Struct.*, **1977**, *7*, 265.
- [28] Spagna R.; Zambonelli L. *J. Chem. Soc. A*, **1971**, 2544.
- [29] Mura P.; Spagna R.; Zambonelli L. *Acta Cryst., Sect. B*, **1978**, *34*, 3745.
- [30] Bachechi F.; Zambonelli L. *J. Cryst. Spect. Res.*, **1988**, *18*, 277.
- [31] Benedetti E.; Carradini P.; Pedone C. *J. Organomet. Chem.*, **1969**, *18*, 203; Corradini P.; Ganis P.; Pedone C. *Acta Cryst.*, **1966**, *20*, 458.
- [32] Ganis P.; Pedone C. *Rendiconti*, **1965**, *8*, 1462.

- [33] Guggolz E.; Koff M.; Ziegler M.L. *Z. Anorg. Allg. Chem.*, **1983**, 499, 59.
- [34] Kopp M.; Krauth L.R.; Ratka R.; Wiedenhammer K.; Ziegler M.L. *Z. Naturforsch.*, **1980**, 35 b, 802.
- [35] Canty A.J.; Jin H.; Skelton B.W.; White A.H. *Inorg. Chem.*, **1998**, 37, 3975.
- [36] Aye K.T.; Vittal J.J.; Puddephatt R.J. *J. Chem. Soc., Dalton Trans.*, **1993**, 1835.
- [37] McCrindle R.; Ferguson G.; Arsnauld G.J.; McAlles A.J.; Ruhl B.L.; Sneddon D.W. *Organometallics*, **1986**, 5, 1171.
- [38] Braga D.; Grepioni F.; Walther D.; Heubach K.; Schmidt A.; Imhof W.; Görls H.; Klettke T. *Organometallics*, **1997**, 16, 4910.
- [39] Jäger S.; Hazell R.G.; Rasmussen S.E. *J. Chem. Soc., Dalton Trans.*, **1976**, 337.
- [40] Komatsu K.; Kamo H.; Tsui R.; Masuda H.; Takeuchi K. *J. Chem. Soc., Chem. Commun.*, **1991**, 71.
- [41] Stamm E.; Becker K.B.; Engel P.; Ermer O.; Keese R. *Angew. Chem. Int. Ed. Engl.*, **1979**, 18, 685.
- [42] Wicht D.K.; Zhuravel M.A.; Gregush R.V.; Glueck D.S.; Guzei I.A.; Liable-Sands L.M.; Reingold A.L. *Organometallics*, **1998**, 17, 1412.
- [43] Chin-Wing Chen; Ting-Tong Lai; Chi-Ming Che; Shie-Ming Peng *J. Am. Chem. Soc.*, **1993**, 115, 11245.
- [44] Steinborn D.; Geusch M.; Bruhm C.; Davies J.A. *Inorg. Chem.*, **1999**, 38, 680.
- [45] Bonamico B.; Dessy G.; Fares V.; Russo M.V.; Scaramuzza L. *Cryst. Struct. Commun.*, **1977**, 6, 39.
- [46] Nicolaidis A.; Smith M.; Kumar A.; Barnhart D.M.; Borden W.T. *Organometallics*, **1995**, 14, 3475.
- [47] Mole L.; Spencer J.L.; Carr N.; Orpen A.G. *Organometallics*, **1991**, 10, 49; Carr N.; Mole L.; Orpen A.G.; Spencer J.L. *J. Chem. Soc., Dalton Trans.*, **1992**, 2653.
- [48] Höpp M.; Erxleben A.; Rombeck I.; Lippert B. *Inorg. Chem.*, **1966**, 35, 397.
- [49] Minghetti P.; Cinellu N.A.; Steccoro S.; Zucca A.; Manassero M. *J. Chem. Soc., Dalton Trans.*, **1995**, 777.
- [50] Maasarani F.; Davidson M.F.; Wehmen-Ooyevaar I.C.M.; Grove D.M.; van Koten M.A.; Smets W.J.J.; Spek A.L.; van Koten G. *Inorg. Chim. Acta*, **1995**, 235, 327.
- [51] Pregesin P.S.; Wombacher F.; Albinati A.; Lianza F. *J. Organomet. Chem.*, **1991**, 418, 249.
- [52] Casas J.M.; Falvello L.R.; Fornies J.; Martin A. *Inorg. Chem.*, **1996**, 35, 56.
- [53] Johnson D.A.; Cordes A.W.; Fithen-Kelley B.A.; Deese W.C. *J. Coord. Chem.*, **1944**, 32, 1.
- [54] Keeton M.; Mason R.; Russell D.R. *J. Organomet. Chem.*, **1971**, 33, 259.
- [55] Robertson G.B.; Tucker P.A. *Acta Cryst., Sect. C*, **1983**, 39, 1354.
- [56] Bennett M.A.; Chee H.K.; Robertson G.B. *Inorg. Chem.*, **1979**, 18, 1061.
- [57] Villa A.Ch.; Manfredotti A.G.; Guastini C.; Carusi P.; Furlani A.; Russo M.V. *Cryst. Struct. Commun.*, **1977**, 6, 629.
- [58] (a) Al-Juaid S.S.; Carmichael D.; Hitchcock P.B.; Kochschmidt S.; Marinetti A.; Mathey F.; Nixon J.F. *J. Chem. Soc., Chem. Commun.*, **1988**, 1156; (b) Al-Juaid S.S.; Carmichael D.; Hitchcock P.B.; Marinetti A.; Mathey F.; Nixon J.F. *J. Chem. Soc., Dalton Trans.*, **1991**, 905.
- [59] Briggs J.R.; Crocker Ch.; McDonald W.S.; Shaw B.L. *J. Chem. Soc., Dalton Trans.*, **1981**, 575.
- [60] Balashev K.P.; Engelbretsen T.; Kwam P.I.; Martmann-Moe K.; Puzyk M.V.; Songstad J. *Acta Chem. Scand.*, **1996**, 50, 1108.
- [61] Toto S.D.; Olmstead M.M.; Arbuckle B.W.; Bharadway D.K.; Musker W.K. *Inorg. Chem.*, **1990**, 29, 691.
- [62] Plantevin V.; Blosser P.W.; Gallucci J.C.; Wojcicki A. *Organometallics*, **1994**, 13, 3651.
- [63] Albinati A.; Lianza F.; Berger H.; Arz C.; Pregosin P.S. *Inorg. Chim. Acta.*, **1992**, 198-200, 771.
- [64] Henderson W.; Micholson B.K. *Polyhedron*, **1996**, 15, 4015.
- [65] Fanezzi F.P.; Natile G.; Lanfranchi M.; Tiripicchio A.; Pacchioni G. *Inorg. Chim. Acta*, **1998**, 275-276, 500.
- [66] Carty A.J.; Haare J.L.; Patel J.; Pfeiffer M.; Skelton B.W.; White A.M. *Organometallics*, **1999**, 8, 2660.
- [67] Carty A.J.; Honeyman R.T.; Skelton B.W.; White A.M. *J. Organomet. Chem.*, **1992**, 424, 381.
- [68] von Zelewsky A.; Suckling A.P.; Stoeckli-Evans H. *Inorg. Chem.*, **1993**, 32, 4585.
- [69] Gelling A.; Orrell K.G.; Osborne A.G.; Šik V.; Hursthouse B.; Coles S.J. *Polyhedron*, **1996**, 15, 3203.
- [70] McGinnety J.A. *J. Organomet. Chem.*, **1973**, 59, 429.
- [71] Hassan F.S.M.; Higgins S.J.; Jacobsen G.B.; Shaw B.L.; Thornton-Pett M. *J. Chem. Soc., Dalton Trans.*, **1998**, 3011.
- [72] Wurst K.; Striale J. *Z. Naturforsch.*, **1993**, 48b, 425.
- [73] Chooi S.Y.M.; Ranford J.D.; Leung P.H.; Mok K.F. *Tetrahedron Assym.*, **1994**, 5, 1805.
- [74] Liu H.; Tan A.L.; Mok K.F.; Hor T.S.A. *J. Chem. Soc., Dalton Trans.*, **1996**, 4023.
- [75] Baratt E.; Boudreaux E.A.; Demas J.N.; Lenhart P.G.; Lukehart C.M.; McPhail A.T.; McPhail D.R.; Myers J.B. Jr.; Sacksteder L.; True W.R. *Organometallics*, **1989**, 8, 2417.
- [76] Jans J.; Naegeli R.; Venani L.M.; Albinati A. *J. Organomet. Chem.*, **1983**, 247, C37.
- [77] (a) Lydon J.E.; Truter M.R.; Watling R.C. *Proc. Chem. Soc. (London)*, **1964**, 193; (b) Truter M.R.; Watling R.C. *J. Chem. Soc. A*, **1967**, 1955; (c) Lydon J.E.; Truter M.R. *ibid.*, **1965**, 6899.
- [78] Park S.; Roundhill D.M.; Rheingold A.L. *Inorg. Chem.*, **1987**, 26, 3972; *Organometallics*, **1991**, 10, 615.
- [79] Bertani R.; Mozzoni M.; Michelin R.A.; Benetollo F.; Bombieri G.; Castilhi T.J.; Pombieno A.J.L. *Inorg. Chim. Acta*, **1991**, 189, 175.
- [80] Manojlovi-Muir L.; Muir K.W.; Frew A.A.; Ling S.S.M.; Thompson M.A.; Puddhephatt R.J. *Organometallics*, **1984**, 3, 1637; Preddephatt R.J.; Thomson A.A.; Manojlovi-Muir L.; Muir K.W.; Frew A.A.; Brown M.P. *J. Chem. Soc., Chem. Commun.*, **1981**, 805.
- [81] Albinati A.; Chaloupka S.; Eckert J.; Venanzi L.M.; Wolfer M.K. *Inorg. Chim. Acta*, **1997**, 259, 305.
- [82] Lewis J.; Long N.J.; Raitby P.R.; Shields G.P.; Wong W.Y.; Younus M. *J. Chem. Soc., Dalton Trans.*, **1997**, 4283.
- [83] Wong W.Y.; Wong W.K.; Raitby P.R. *J. Chem. Soc., Dalton Trans.*, **1998**, 2761.
- [84] Bruno R.A.; Farrar D.H.; Irwin J.J. *Inorg. Chim. Acta*, **1991**, 181, 65.
- [85] Leoni P.; Manetti S.; Pascquali M.; Albinati A. *Inorg. Chem.*, **1996**, 35, 6045.
- [86] Duran M.; Clegg W.; Fraser K.A.; Gonzalez-Duarte P. *Inorg. Chim. Acta*, **2000**, 300-302, 790.
- [87] Klevstova R.F.; Yurchenko E.N.; Glinskaya L.A.; Burgina E.B.; Eremenko N.K.; Bkakin V.V. *Zh. Strukt. Khim.*, **1985**, 26, 84; *Engl. Ed.*, p. 216.
- [88] Ebert K.H.; Massa W.; Donath H.; Lorberth J.; Seo B.S.; Herdtweck E. *J. Organomet. Chem.*, **1998**, 559, 203.
- [89] Raper G.; McDonald W.S. *J. Chem. Soc., Dalton Trans.*, **1972**, 265.
- [90] Kernbach U.; Fehlhammer W.P. *Inorg. Chim. Acta*, **1995**, 235, 299.
- [91] Stang P.J.; Kowalski M.H. *J. Am. Chem. Soc.*, **1989**, 111, 3356.
- [92] Chen J.T.; Yeh Y.S.; Yang Ch.S.; Tsai F.Y.; Huang G.L.; Shu B.Ch.; Huang T.M.; Chen Y.S.; Lee G.H.; Cheng M.Ch.; Wang Ch.Ch.; Wang Y. *Organometallics*, **1994**, 43, 4804.
- [93] Manojlovi-Muir L.; Muir K.W. *J. Chem. Soc., Dalton Trans.*, **1974**, 2427.
- [94] Lin I.J.B.; Kao L.T.C.; Wu F.J.; Lee G.H.; Wang Y. *J. Organomet. Chem.*, **1986**, 309, 225.
- [95] Gianini M.; Ferster A.; Haang P.; von Zelewski A.; Stoeckli-Evans H. *Inorg. Chem.*, **1996**, 35, 4889.
- [96] Mura P.; Spagna R.; Zambonelli L. *J. Organomet. Chem.*, **1977**, 142, 403.
- [97] Mura P.; Spagna R.; Zambonelli L. *Acta Cryst., Sect. B*, **1976**, 32, 2532.