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Crystallographic and structural characterisation of heterometallic platinum compounds: Part I. Heterobinuclear Pt compounds.

Review Article

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Abstract: This review covers almost 290 heterobinuclear Pt derivatives. When the heterometals (M) are non transition and the binuclear are found both with and without a metal to metal bond. Where M is a transition metal or actinide, only those with a metal-metal bond have been included here. There are thirteen non-transition metals (Sn, Hg, Ge, Sb, Tl, Zn, Pb, Cd, Na, K, Ga, Ca and In). The shortest Pt-M bond distance is 235.2(1) (Pt-Ge). There are eighteen transition metals (Fe, W, Rh, Re, Pd, Ag, Ir, Mo, Mn, Re, Co, Cu, Cr, Au, Ni, Ti, Ta and V). The shortest Pt-M bond distance is 249.5(2) pm (Pt-Cr). There is one example of an actinide, Pt-Th at 298.4(1) pm. The Pt atom has oxidation numbers 0, +2 and +4. The Pt coordination geometries include square planar (most common), trigonal bipyramidal, pseudo octahedral (Pt(IV)) and a few prevalently capped trigonal prismatic seven coordinate species. There are at least two types of isomerism distortion and polymerisation. Factors affecting bond lengths and angles are discussed and some ambiguities in coordination polyhedra are outlined.

Keywords: *Platinum • Heterobinuclear • Structure • Isomers • Trans effect.*

1. Introduction

It is well known that the most frequent oxidation states of platinum are +2 and +4. The kinetic inertness of Pt(II) complexes has led to their extensive use in studies of geometrical isomerism and reaction mechanism. Also, in the divalent state platinum shows a class-B preference for CN^- and ligands with N-donor atoms or heavy donor atoms rather than oxygen or fluorine. By contrast, Pt(IV) is closer to a class-A acceptor and is frequently reduced to Pt(II) by the class-B donor ligands containing heavier atoms such as P and As. The coordination and organometallic chemistry of platinum is extensive and varied, including involvement of unsaturated hydrocarbons.

Up to the end of 1999 numerous structural studies have been made, including over two thousand five hundred coordination complexes [1-6], and over one thousand organometallic compounds (reviews in progress). The aim of this review is to categorise the crystallographic and structural data for the binuclear heterometallic compounds of platinum. Material has been primarily obtained from the Cambridge Crystallographic Data Base up to the end of 2002. Included are both non-transition metals (with and without Pt-M bonds), transition metals (only with Pt-M bonds), and Pt-Th (actinide) compounds. The structures have been organised on the basis of the Periodic Group of the heterometal atom, and on increasing Pt-M distance.

2. Heterobinuclear (PtM) compounds

2.1 Compounds with non-transition metals

There are ninety binuclear heterometallic derivatives in which M is a non-transition metal and the data for these are listed in Table 1. There are over sixty five derivatives with a direct Pt-M bond and no ligand bridging the two metals. In another twelve derivatives [32,54-65] in addition to a Pt-M bond there is also one or more ligand bridges. In the remaining thirteen examples [61,63,66-75] the only link between Pt and M is *via* one or more bridging ligands.

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Most of the examples are yellow, with four types of crystal class; monoclinic (55 examples), triclinic (22), orthorhombic (12) and tetragonal (1 example). The shortest Pt-M distance is for M = Ge [7] at 235.2(1) pm, and the structure of this compound is shown in Fig. 1 as an example of this type of compound. The Pt(IV) atom is pseudo-octahedral (PtN_2C_2ClGe) and the Ge(II) atom is tetrahedral ($GeCl_3Pt$). The Pt-Cl distance trans to the methyl group is 245.2(3) pm.

The structure of a Pt-Sn complex [32] is shown in Fig. 2 as an example which has both a Pt-Sn bond (255.78(7) pm) and a ligand bridge. The 5-membered {Pt-SnC=CSe} ring de*via*tes only slightly from planarity (torsion angles of -8.6° for Pt-Se-C=C and 9.3° for Pt-Sn-C=C). The Pt-N(2) distance of 224.4(7) pm trans to Sn is longer than the Pt-N(1) value of 214.4(6) pm trans to methyl because of the very high trans influence of the Sn atom.

The structure of orthorhombic Pt-Zn complex is shown in Fig. 3 [66], and is characterised by a 6-membered {PtCNZnNC} ring with boat conformation involving the 2-pyridyl and amidino ligands. A distorted square planar geometry occurs around the Pt centre (PtC_2P_2) with a distorted tetrahedral geometry around the Zn atom (ZnN_2Cl_2). The Pt-Zn separation of 323.8(1) pm is considered too large to permit any significant Pt-Zn bonding to be present.

The data in Table 1 show that the Pt atom shows coordination numbers of three [9], five [22,25,28,29,39,57-61], six [7,8,20,23,26,27,30-33,39,41,51,54], seven [44] and eight [40]. All remaining complexes have four-coordinate Pt atoms with varying degrees of distortion from square-planar. The ligands range from unidentate, though bi-, tri-, tetra-, penta- and octadentate. The most common donor atoms are P, C, Cl and N. The mean Pt-P bond length increases with the size of the P-donor ligand in the order: 226.5 pm (PEt_3) < 227.5 pm ($PPhMe_2$) < 228.8 pm (PPh_3). All of them increase as a result of the trans influence (of Ge, Sn or C) in the order: 233.0 pm ($PPhMe_2$) < 234.3 pm (PPh_3) < 234.6 pm (PEt_3). The mean Pt-L bond lengths follow this trend; L = Cl (233.7 *vs.* 245.8 pm); L = Br (241.7 *vs.* 250.9 pm). The mean Pt-C bond length increases in the order: 188 pm (CO) < 200 pm (CN or CNL) < 205.5 pm (Ph) < 206 pm (Me).

The mean Pt-L(unidentate) value increases in the order: 204 pm (CL) < 215 pm (NL) < 230.5 pm (PL) < 240.3 pm (Cl) < 247.2 pm (Br) < 278.5 pm (I). This reflects the radii of the coordinating atom except in the cases of N-donors or the Cl atom. For homo-bidentate ligands the order is: 212 pm (CL) < 213 pm (NL) < 228.0(PL) < 240.0 pm (SL). For homo-tridentate ligands the order is: 219 pm (CL) < 232 pm (PL).

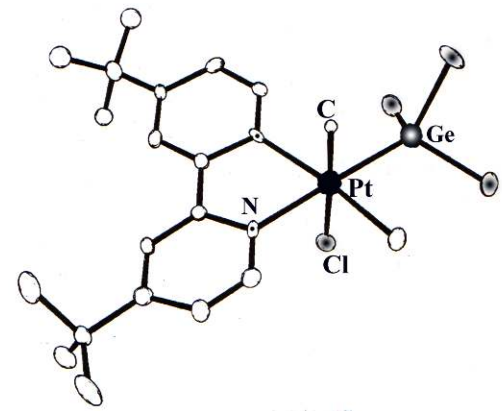

Figure 1. Structure of [(η^2-4,4'-Bu^{t}bpy)(Me)$_2$ClPtGeCl$_3$] [7]

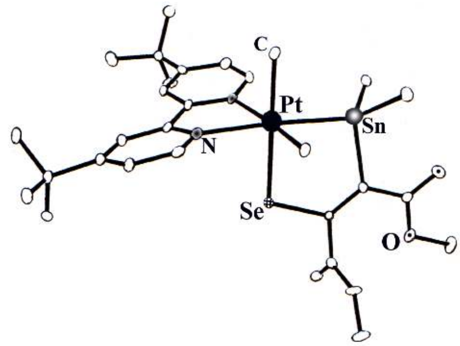

Figure 2. Structure of [(η^2-4,4'-Bu^{t}bpy(Me)$_2$Pt{μ-η^2-sec(CO$_2$Me)=C(CO$_2$Me)}Sn(Me)$_2$ [32]

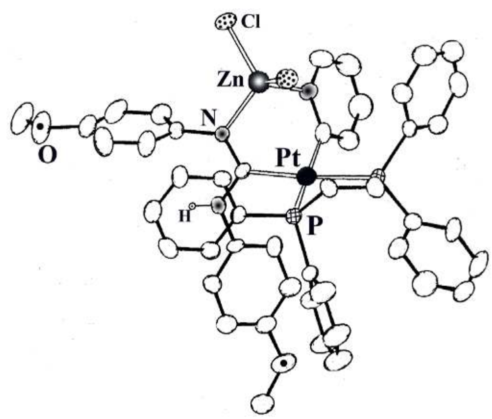

Figure 3. Structure of (η^2-dppe)Pt(μ-η^2-C$_5$H$_4$N){μ-η^2-C(OEt)(NHC$_6$H$_4$PMe-4}ZnCl$_2$ [66]

It is noted that in the heterobidentate ligands, non-chelating to Pt, where there is an O-donor and a C-, N- or S-donor, the O-site is coordinated to the heteroatom while the other site is coordinated to the Pt atom. However, when the heterobidentate has N plus C or C plus P donor sites, chelating to the Pt atom does occur. Chelation to Pt also occurs in similar circumstances with heterotridentate, heterotetradentate and heteropentadentate ligands.

In the examples with chelating ligands, electronic and steric factors both play a role in the resultant geometry and is reflected in the L-Pt-L ring angles of the respective metallocycles. The mean L-Pt-L angle for the 3-membered rings opens in the order: 39.5° (C,C) < 43.3° (C,B) < 48.3° (B,B) < 48.5° (C,S). This reflects the radii of the donor atoms. For the 4-membered rings the order is: 68° (CCP) < 73.6° (SCS). In the 5-membered rings the order is: 75.7° (NC=CN) < 80.5° (NC_2N) < 86.5° (PC_2P). Some complexes containing Pt-Ge bonds generate 4-, 5- and 6-membered rings with values: 64.7° (PtCOGe) < 66.0° (PtNCGe); 76.5° ($PtNC_2Ge$) < 82.3° (PtSNOGe); and 77.0° (PtOCNOGe).

A summary of the Pt-M distances for the heterobinuclear complexes with non-transition metals is given in Table 1A. There are a variety of structural forms with metal-metal bonds and with no direct Pt-M contact.

The heterometals show a variety of stereochemistry with coordination numbers varying from one (Tl), two (Hg, Tl Sb), three (G+e, Hg, In, Sb), four (Ge, Sb, Sn, Pb, Hg, Zn), five (Cd, Tl, Pb), six (Sn, Tl, Zn, Ca, Hg, Na, K), and eight (Pb).

There are four complexes [26,35,50,63] which contain two crystallographically independent molecules differing mostly by degree of distortion of the M-L distances and L-M-L angles. These represent examples of distortion isomerism [76].

There are also examples containing, within the same crystal, a hetero binuclear plus an M monomer [26,39]; a hetero dimer plus an M dimer [64] together with examples of polymerisation isomerism.

2.2 Compounds with transition metal

2.2.1 M = Cu, Ag or Au

The data for platinum complexes with these metals are listed in Table 2. There are six derivatives with copper [40,77,83], ten with silver [79,80-82,84,86,87,89] and five with gold [40,78,85,88,90]. The structures are referenced in order of increasing Pt-M bond length.

In four green $Pt^{II}Cu^{II}$ derivatives [77] a $Pt(MeNH_2)_2$ and a CuL_1L_2 moieties are held together by two μ-η^2-1-methylcytosinato-N3,N3(-1) ligands. The Pt to Cu dative bonds range from 250.1(2) to 255.6(2) pm. In a yellow PtCu derivative [40] the Pt-Cu bond distance is 260.58(5) pm with $(Et_3P)_2Pt$ and $Cu(PPh_3)$ units are bridged by the $CB_{10}H_{11}$ ligand. In another yellow PtAu derivative [40] the $CB_{16}H_{11}$ ligand serves as a bridge between Et_3Pt and $Au(PPh_3)$ moieties with a Pt-Au bond length of 261.12(7) pm. Four derivatives, Pt-Au [82] and Pt-Ag [79,80] have the Pt and M moieties linked only by the single Pt to M dative bond. Three derivatives (M = Au [81,85] and Ag [82]) have both a direct Pt-M bond plus a single bridging hydrogen atom, with mean Pt-H-M bridge angle of 103°. A green Pt-Cu binuclear has $(H_3N)_3Pt$ and $Cu(H_2O)_2$ with a direct Pt-Cu bond of 276.5(3) pm length, plus two bridging μ-1-methyluracilato-N^3,O^4 (-1) ligands. The N coordinates to Pt and the O atom to Cu.

Table 1A. Summary of the Pt-M bond distances in Hetero- binuclear Platinum Compounds (M = non-Transition)

Pt-M	Range [ref], pm	Average, pm
-Ge	235.2(1) [7] – 247.15 [10]	242.5
-Ga	243.8(1) [14]	
-Sb	246.3(2) [17] – 264.1(1) [53]	255.9
-Sn	248.6(5) [18] – 265.1(1) [55]	266.0
-Hg	251.2(1) [20] – 283.5(1) [59]	265.7
-In	260.12(2) [47]	
-Cd	261.01(8) [49] – 263.89(8) [49]	262.5
-Tl	262.96(3) [51] – 299.4(1) [65]	287.4
-Pb	264.2(1) [54] – 269.8(10) [56]	267.0
-Zn	276.0(1) [58]	
-Ca	296.0(5) [64]	

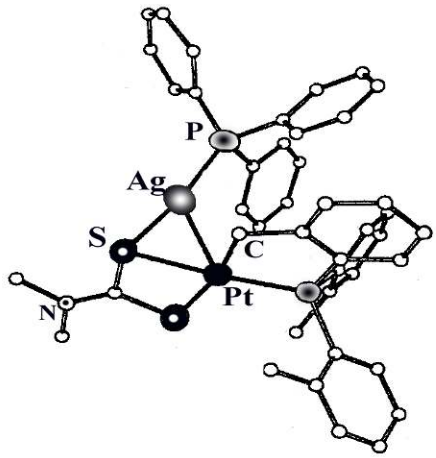

Figure 4. Structure of [(η^2-mppm)Pt(μ-η^2-S_2CNMe_2)Ag(PPh_3)] [87]

Two pale yellow PtAg binuclear with metal bond distances of 278.2(1) [84] and 279.6(2) pm [86] are additionally bridged by a single Cl atom with Pt-Cl-Ag bridge angles of 67.24(6)° and 71.0(1)°, respectively.

The structure of yellow Pt-Ag binuclear [87] is shown in Fig. 4. The Pt atom exhibits a distorted square pyramidal geometry, with Pt, C and P atoms of the C/P ligand and both S atoms of the S_2CNMe_2 ligand located in the basal plane. The Ag atom of the $[Ag(PPh_3)]^+$ fragment is in the apical position. The angle between the Pt-Ag vector (Pt-Ag = 287.5(1) pm) and the perpendicular to the basal plane is 29.5°. The Pt and Ag fragments ($Pt(mppm)(S_2CNMe_2)$) and ($Ag(PPh_3)$) share one S atom of the distorted dithiocarbamate group, leading to a very acute Pt-S(1)-Ag angle of 70.6(1)°.

The complex $[(PhC{\equiv}C)_2Pt(\mu\text{-}\eta^2\text{-dppm})_2Au]^+$ cation consists of a square planar P-Pt-$(C{\equiv}Ph)_2$-P unit and a linear P-Au-P moiety with intramolecular Pt-Au distance of 291.0(1) pm [88]. In another Pt-Au binuclear [90] the

7,8-Me_2-nido-CB_9H_9 cage is bonded to both metal atoms *via* the open pentagonal CCBBB face, with Pt-Au distance of 300.0(1) pm.

The data in Table 2 shows the mean Pt-M bond distance to increase in the order: 258.3 pm (range 250.1(2) [77] to 276.5(3) pm [83])for M = Cu < 274.8 pm (range 263.7(1) [79] to 294.5(1) pm [89]) for M = Ag < 278.6 pm (range 261.12(7) [40] to 300.0(1) pm [90]) for M = Au.

2.2.2 Ti, V, Ta, Cr, Mo and W

The data for these compounds are listed in Table 3, with structures listed in order of increase in length of the Pt-M bond. In two cases of composition (η^4-cod)(Ph)PtM$(CO)_3$(η^5-cp) (M = Mo [120] or W [121]), the metal complex fragments are held together only by the Pt-M bond (Pt-Mo = 283.20(12) pm, and Pt-W = 284.35(71) pm). In the remainder derivatives there is a direct Pt-M bond plus one or more ligand bridges involved.

Three examples [91] have a common lantern type structure in which four pyridine-2-thiolate(-1) ligands bridge the two metal atoms. The Pt(II) atom has a square planar coordination with four S atoms. The Cr(III) or V(IV) atoms are coordinated by four N atoms and a Cl or O atom in a square pyramidal fashion, with the Cl or O atom in the apical position. The asymmetrical unit of orange-red [Pt(μ-η^2-4-mpyt)$_4$CrCl] [91] has two crystallographically independent molecules with Pt-Cr bond distances of 249.5(2) and 249.9(2) pm. These are the shortest Pt-M bonds in this series. The two independent molecules are combined to form a pair through two intermolecular Pt···S interactions at an average distance of 310 pm. In yellow [Pt(μ-η^2-4-mpyt)$_4$Cr(OH)] the Pt-Cr bond distance is 250.9(3) pm. A longer Pt-V bond distance of 260.4(7) pm is found in the [Pt(μ-η^2-4-mpyt)$_4$VO] analogue [91].

In two orange PtW derivatives [92,93] two CO groups serve as bridges between the two metal atoms. The Pt-W bond distances are the same at 260.2(1) pm and the mean Pt-C-W of 76.0°.

There are several examples in which a CL ligand (commonly μ-CC_6H_4Me-4 or derivatives) acts as a bridge, PtCr [94], PtW [99-101,105,116,118,123] and PtTa [132], with a mean Pt-C-M bridge angle of 80.8°. The Pt-Cr bond distance of 264.6(7) pm [94] is shorter than the Pt-W values which range from 275.1(1) [99] to 286.1(1) pm [123]. The Pt-Ta bond distance is not available [132].

In a Pt/W derivative [95] with dihydro bridges the Pt-W bond length is 266.3(1) pm. In another four derivatives [96,98] the Pt-W bonds (272.0(1), 272.8(1) twice and 273.8(1) pm) are spanned by the p-tolylmethylidene [96] or 2,6-dimethyltolylmethylidyne [98] group and by a C_2B_9 fragment. The latter is coordinated to the W atom *via* the open pentagonal face of the nido-icosahedral cage, and bridges to the Pt atom through an exopolyhedral B-Pt σ-bond (average 212 pm).

Another six derivatives have Pt-W [97,104,109,110,125] or Pt-Mo [111] bonds. The Pt-W distances range from 272.0(1) [97] to 287.1(1) pm [125], and the Pt-Mo bond distance is 280.6(2) pm. The Pt-M bonds are also spanned by a CO group and p-tolylmethylidene [97,104,109,110], H_2C=CCO_2Me [111] or HCNEt_2 [125], with mean Pt-C-M bridge angle of 81.5°.

There are two orange-red Pt/Ti derivatives [106] in which Pt-Ti bonds (277.6(1) and 296.2(2) pm) are spanned by μ-CH_2 and μ-CH_3 groups with a mean Pt-C-Ti bridge angle of 75.6° and 86.6°, respectively. A brown Pt/Cr derivative [117] has a Pt-Cr bond length of 282.0(1) pm and is spanned by a CO group and a PPh_2 group with Pt-P-Cr bridge angle of 75.93(6)°. The Pt-C-Cr bond angle is not given. Two yellow Pt/W [102] and one Pt/Mo derivative [103] have Pt-M bonds of 276.4(1) and 279.5(1) pm [102] and 276.6(1) pm [103], spanned by two PPh_2 groups with mean Pt-P-M bridge angle of 71.4°.

Two sulphur atoms span the Pt-W bonds in a purple [107] and two yellow [124,131] species. As the Pt-W bond length increase the Pt-S-W angle opens: 277.92(6) pm and 75.3° < 286.22 pm and 77.2° < 294 pm and 79.6°.

There are two red Pt/Ti derivatives [108,119] in which the Pt-Ti bond is spanned by two C=CBu^t ligands. The mean Pt-C-Ti bridge angels open with increasing Pt-Ti distance; 80.8° and 278.9(3) pm [108] < 83.2° and 283.1(2) pm [119].

In a yellow Pt/W derivative [112] the Pt-W bond (281.0(1) pm is spanned by a μ-PPh_2 ligand with the Pt-P-W bridge angle of 74.9°. Two orange Pt/W derivatives [113,115] with Pt-W bonds of 281.0(2) and 281.8(3) pm, respectively, are spanned by μ-inst-C and μ-η^2-dppm-P,P' [113] or μ-C(OMe)C_6H_4Me-4 and μ-η^2-dppm-P,P' [115] ligands. The Pt-C-W bridge angles are 82.2(4)° [113] and 77.3(9)° [115].

The structure of a red Pt/Mo derivative is shown in Fig. 5. The Pt-Mo bond of 281.4(1)° is spanned by the nido-$C_2B_{10}H_{10}Me_2$ cage such that the latter is η^6-coordinated *via* a three-centre, two electron, B(5)H to Pt bond. The H atom involved is β to the carbons in the CBCBB face of the cage ligated to the Mo atom. In another red Pt/Mo derivative [122] the Pt-Mo bond of 284.5(1) pm is spanned by a CO and a μ-η^2-Ph_2Ppy-P_1N ligand. In a yellow derivative, a hydrido bridge and a p-tolylmethylidene bridge span the Pt-W bond of 289.5(1) pm, with Pt-X-W bridge angles of 111° (X = H) and 83.0(3)° (X = C) [126].

Two μ-η^2-dppm-P,P' ligands span Pt-M bonds in the red derivatives with a Pt-M bond length of 290.2(2) pm (M = W) [127] and 291.2(4) pm (M = Mo) [129]. With two μ-η^2-F_2PN(Me)PF_2 ligands as bridges [129] the Pt-Mo

Table 1. Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
[(η²-4,4'-Bu$^t_2$bpy)(Me)$_2$Cl. PtGeCl$_3$]1.5CH$_2$Cl$_2$ (yellow) at 200K	m P2$_1$/c 4	1419.0(1) 2006.1(1) 1151.5(1)	 106.342(2)	$Pt^{IV}N_2C_2ClGe$ $Ge^{II}Cl_3Pt$	η²N[b] 212(1,2) C$_{Me}$ 206(3,1) Cl 245.2(3) Cl not given	Ge[b] 235.2(1)	not given	7
(η²-CH$_2$=CH$_2$) (η²-Me$_2$-phen) ClPtGe(Ph)$_2$Cl at 223(2)K	m P2$_1$/c 4	1352.6(4) 1336.6(8) 1661.7(10)	 102.59(2)	$Pt^{IV}N_2C_2ClGe$ GeC_2ClPt	η²N 220.5(7,6) η²C206.7(9,10) Cl 245.3(2) C$_{Ph}$ 196.6(4,6) Cl 245.3(2)	Ge 236.4(1)	N,N 73.8(3)[c] Cl,Ge 177.29(8) C,Cl 105.3(2,5.0) C.Pt 116.3(2,2.0) Cl,Pt 107.69(8)	8
(Et$_3$P)$_2$Pt {μ-η²-C(O)O} Ge{N(tms)$_2$}$_2$ (colourless)	or Pbca 8	1552.0(2) 1361.8(2) 3715.6(6)		PtP_2CGe GeN_2OPt	P$_{Et}$ 230.9(2) 234.6(2) C 208.6(9) N 187.3(6,9) O not given	Ge 241.97(9)	P,P 98.97(8) P,C 89.1(2) 167.0(3) P,Ge 105.92(6) 154.87(6) C,Ge 65.8 N,N 110.0(3) N,O 101.9(3,3.6) N,Pt 24.0(2,6) O,Pt 81.7(2)	9
(Et$_3$P)$_2$PtGe {N(tms)$_2$}$_2$ (colourless)	m P2$_1$/c 4	1877.0(3) 1237.6(2) 1700.05(2)	 102.02(1)	PtP_2Ge GeN_2Pt	P$_{Et}$ 229.3(4,8) N 191(1,1)	Ge 242.2(2)	P,P 106.8(1) P,Ge 92.7(1) 159.0(1) N,N 106.9(4) N,Pt 117.1(3,4.1)	9
(Et$_3$P)$_2$Pt{μ-η²-N(Ph)O}. Ge{N(SiMe$_3$)$_2$}$_2$ (orange) at 178(2)K	m C2/c 8	4292.8(3) 1137.3(1) 1935.0(1)	 1115.326	PtP_2NGe GeN_2OPt	P$_{Et}$ 224.9(2) 235.6(2) μN$_L$ 208.8(5) N 188.1(4,4) μO$_L$ 182.0(4)	Ge 242.14(7)	P,P 96.08(6) N,P 97.32(13) N,Ge 66.00(13)[d] P,Ge 99.76(5) N,N 113.8(2) N,O 102.5(2,2.3) N,Pt 121.33(14,17)	10
(Et$_3$P)$_2$(Ph)PtGe(Ph)$_2$(OH) (colourless)	or Pnma 4	1862.1(10) 1514.6(10) 1124.5(8)		$Pt^{II}P_2CGe$ GeC_2OPt	P$_{Et}$ 232.3(5,6) C$_{Ph}$ 204.3(13) C 197.5(12,0) O 183.8(12)	Ge 243.3(2)	P,P 99.6(2) P,C 88.4(4) P,Ge 91.6(1) 168.8(2) C,Ge 80.4(4) C,Pt 118.5(3) O,Pt 115.0(4)	11
(Et$_3$)$_2$Pt(μ-η²-CH2O). Ge{N(SiMe3)2}2 (yellow)	m P2$_1$/n 8	2244.53(2) 1567.70(2) 2331.87(1)	 110.84	PtP_2CGe GeN_2OPt	P$_{Et}$ 230.32(6) 232.41(6) C 210.9(2) N 189.2(2,3) O 183.4(2)	Ge 243.68(3)	P,P 96.94(2) C,Ge 64.75(6)[d] N,N 108.44(9) O,Pt 85.22(5)	12
(PMe$_2$Ph)$_2$(Et)PtGe(Ph)$_3$ (colourless)	tr_ P1 2	1054.9(3) 1919.5(4) 892.0(2)	 108.93(2)	PtP_2CGe GeN_2C_2Pt	P 230.9(2,2) C$_{Et}$ 213.4(9) not given	Ge 243.7(1)	P,P 96.76(8) P,C 84.1(2) 174.8(2) P,Ge 94.35(5) 166.50(6) C,Ge 85.6(2)	13
(η²-dcpe)η¹-npe)Pt. Ga(η¹-npe)$_2$ (yellow)	m P2$_1$/c 4	1789.6(1) 1124.9(1) 2288.7(1)	 98.48(1)	PtP_2CGa GaC_2Pt	η²P$_L$ 225.2(4) 231.7(3) η¹C 213(1) η¹C$_L$201(1,1)	Ga 243.8(1)	P,P 86.1[c] P,C 92.3 P,Ga 95.7 C,Ga 86.9 not given	14
(PMe$_2$Ph)$_2$(Me)PtGe(Ph)$_3$	tr_ P1 2	1168.3(3) 1397.9(2) 1145.3(5)	109.37(2) 113.36(3) 82.88(2)	PtP_2CGe GeC_3Pt	ηP 230.8(2) 233.0(1) ηC$_{Me}$ 212.7(5) PhC not given	Ge 244.95(7)	P,P 94.28(5) P,C 87.0(2) 178.2(2) P,Ge 93.41(4) 166.48(4) C,Ge 85.6(2) not given	15
(Ph$_3$P)$_2$(H)PtGe(Ph)$_3$ (colourless)	or P2$_1$2$_1$2$_1$ 4	1352.23(6) 1781.2(2) 1875.2(2)		PtP_2HGe GeC_3Pt	P$_{Ph}$ 229.17(8) 230.82(8) H not given C$_{Ph}$ not given	Ge 244.00(4)	P,P 104.92(3) P,Ge 95.20(2) 159.27(2) not given	16
[(Et$_3$P)$_2$Pt{μ-η²-N(Ph)C(O)- N(Ph)O}Ge{N(SiMe$_3$)$_2$}$_2$]. 1.5C$_6$H$_6$ (colourless) at 153(2)K	m P2$_1$/c 4	1527.84)4) 1696.14(4) 2213.74(6)	 104.7243(8)	PtP_2NGe GeN_2OPt	P$_{Et}$ 226.92(11) 237.76(12) N 211.2(3) N 189.4(3,11) O 186.7(3)	Ge 245.62(5)	P,P 94.46(4) P,N 89.42(10) P,Ge 101.57(3) N,Ge 76.47(10)[e] N,N 105.6(2) N,O 96.85(14,85) N,Pt 124.39(11,2.4) P,Pt 99.44(9)	10

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
$Br_2(PPh_3)PtSb(Ph)_3$ **(yellow)**	tr P1 2	987.4(1) 1062.0(2) 1831.2(4)	86.22(1) 77.14(1) 70.90(1)	$PtBr_2PPt$ SbC_3Pt	Br 257.8(3,5) P_{Ph} 225.5(7) PhC not given	Sb 246.3(2)	Br,Br 88.12(9) Br,P 92.98(2) 177.41(2) Br,Sb 170.9(9) not given	17
$(Ph_3P)_2(\eta^1$-dpb)$PtGe(Me)_3$ **(colourless)**	or Pbca 8	1618.9(1) 1936.0(1) 259.11(2)		PtP_2BGe GeC_3Pt	P_{Ph} 230.4(1) 237.7(1) η^1B 213.9(6) MeC not given	Ge 247.0(1)	P,P 99.25(5) P,B 87.0(2) 172.5(2) P,Ge 95.03(4) 165.72(4) B,Ge 78.7(2) not given	16
$(Et_3P)_2Pt\{\mu$-η^2-$S(O)_2N(Ph)O\}$. **$Ge\{N(SiMe_3)_2\}_2].3C_6H_6$** **(colourless)** **at 158(2)K**	or $Pna2_1$ 16	2034.44(1) 2150.72(4) 4448.59(6)		PrP_2SGe GeN_2OPt	P_{Et} 230.7(3) 237.3(3) S 231.9(3) N 188.1(9,8) O 186.1(7)	Ge 247.15(11)	P,P 96.06(10) P,Si 89.78(9) P,Ge 170.72(8) S,Ge 82.25(7)[c] N,N 113.7(4) N,O 99.4(3,4) N,Pt 119.6(3,3.5) O,Pt 98.2(2)	10
$(PPh_3Bz)_2[Br_3PtSnBr_3]$ **at 200K**	tr P1 2	1104.6(7) 1416.4(9) 2254.9(10)	89.44(4) 83.32(5) 68.31(5)	$PtBr_3Sn$ $SnBr_3Pt$	Br 242.2(3,9) 247.8(4) Br 250.2(4) 253.0(4,3)	Sn 248.6(5)	Br,Br 91.06(12,85) Br,Sn 88.95(10,31) Br,Br98.26(14,1.51) Br,Pt114.16(13,4.34)	18
$[Et_3P)_2Pt(\mu$-η^2-$OCH_2N(Ph)O\}$. **$Ge\{N(SiMe_3)_2\}_2].C_6H_6$** **at 158(2)K**	tr P1 4	1434.090(1) 1805.04(3) 2096.19(3)	113.736(1) 91.021(1) 98.8190	PtP_2OGe GeN_2OPt	P_{Et} 229.1(3) 238.4(2) O 210.6(7) N 194.1(8,12) O 190.9(6)	Ge 248.74(9)	P,P 102.40(9) P,O 79.2(2) P,Ge 101.25(7) O,Ge 77.0(2)[e] N,N 106.5(3) N,O 99.2(3,3) N,Pt 121.8(2,5.9) O,Pt 102.9(2)	10
$[(\eta^4$-4,4'-$Bu^tbpy)(Me)_2Cl$. **$PtSnCl_3][Me_2SnCl_2Me_2SnO]_2$.** **$C_2H_4Cl_2$** **(yellow)** **at 200K**	m C2/m 4	2089.22(6) 1411.44(5) 1702.89(6)	 124.491(2)	$Pt^{IV}N_2C_2ClSn$ $SnCl_3Pt$	ηN not given C_{Me} not given Cl 238.2(2) Cl 233.2(2,0) 234.8(2)	Sn 249.32(7)	not given Cl,Cl 101.4(1,1.7) Cl,Pt 116.72(7,1.46)	7
$Br_3PtSb(Ph)_3$ **(yellow)**	m C2/c 8	1492.6(2) 1149.5(2) 3619.1(4)	 97.71(2)	$PtBr_3Sb$ SbC_3Pt	Br 241.2(4,20) 247.1(4) C_{Ph} 212.9(2)	Sb 249.6(2)	Br,Br 91.7(1,2) 179.0(1) Br,Sb 87.3(1) 177.8(1) not given	17
$(Et_3P)(\eta^1$-bao)$(Cl)PtSnCl_3$ **(yellow)**	m $P2_1/c$ 4	1594.5 1010.6 1808.9	 106.67	PtNClPSn $SnCl_3Pt$	ηN 209.7(7) Cl 232.5(3) P_{Et} 224.2(3) Cl 234.0(3,10)	Sn 250.1(1)	N,Cl 87.0(2) N,P 175.4(2) N,Sn 89.1(2) Cl,P 88.3(1) Cl,Sn 175.8(1) P,Sn 95.6(1) not given	19
$(\eta^2$-damp$)_2Pt(\mu$-η^2-ac). **$Hg(\eta^1$-ac)** **(yellow)**	or Pccn 8	1481.1(6) 1731.8(6) 1857.8(6)		$Pt^{II}N_2C_2OHg$ HgO_2Pt	μηN 227(1,5) μηC 202(1,0) η^1O 215(1) η^1O 210(1) η^2O 262(1)	Hg 2513(1)	N,N 102.2(3) C,C 93.0(3) N,C 89.6(2,6)[c] 99.4(3) N,O 86.9(4,5.7) N,Hg 90.1(2) C,Hg 88.0(3,6) O,Hg 93.3(3) O,O 103.9(3) O,Pt 80.5(2) 172.3(2)	20
$(Et_3P(p$-Clan$)(Cl)PtSnCl_3$ **(yellow)**	m $P2_1/n$ 4	1063.1(6) 921.4(4) 2157.6(4)	 90.77(3)	PtNClPSn $SnCl_3Pt$	N 215.2(11) Cl 233.1(3) P 223.3(4) not given	Sn 251.4(1)	N,Cl 85.0(3) N,P 173.0(4) Cl,P 88.0(1) N,Sn 92.0(3) Cl,Sn 174.3(1) P,Sn 95.0(1) not given	21
$(\eta^2$-4,4'-$Bu^t_2bpy)(Me)_2Cl$. **$PtSn(Ph)Cl_2$** **(yellow)** **at 200K**	tr P1 2	1119.75(6) 1211.88(6) 1258.65(6)	102.572(2) 112.859(2) 102.488(3)	$Pt^{IV}N_2C_2ClSn$ $SnCl_2CPt$	ηN not given C_{Me} not given Cl 243.3(2) C_{Ph} 213.0(4)	Sn 251.86(6)	not given Cl,Cl 102.71(9) Cl,C 102.3(1,1.2) Cl,Pt 110.64(7,2.4) C,Pt 125.6(1)	7

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
[η⁴-N($CH_2CH_2PPh_2$)$_3$}.PtHg(Me)]BPh_4	m $P2_1/n$ 4	3487.2(9) 1734.0(6) 1078.1(4)	 96.1(1) 	PtP_3NHg HgCPt	ηP 230.9(5) ηN 223.5(15) C_{Me} 220(3)	Hg 253.1(1)	P,P 119.4(14) N.,Hg 176.6(4) C,Pt 175.7(7)	22
(η²-4,4'-Bu$^t_2$bpy)(Me)$_2$Cl.PtSn(Ph)$_2$Cl (yellow)	tr P$\bar{1}$ 4	1280.51(5) 1359.18(6) 2121.23(5)	97.975(2) 9629,3(2) 110.609(2)	$Pt^{IV}N_2C_2ClSn$ SnC_2ClPt	ηN not given C_{Me} not given Cl 247.6(3) C_{Ph} 215.1(6,2) Cl 239.2(3)	Sn 253.19(7)	not given C,C 110.1(3) C,Cl 102.0(2,9) C,Pt 117.0(2,3.5) Cl,Pt 106.35(7)	7
(η²-2,9-Me$_2$phen)(η²-CH_2=CH_2).ClPtSn(Ph)$_2$Cl (pale yellow)	m $P2_1/n$ 4	1385.8(8) 1373.0(6) 1682.0(8)	 102.44(5) 	PtN_2C_2ClSn SnC_2ClPt	ηN 220(1,1) ηC 208(1,1) Cl 247.8(2) C_{Ph} 212(1,1) Cl 239.3(3)	Sn 253.4(1)	N,N 76.3(3) C,C 39.6(5)[f] N,Sn 89.2(2,8) C,Sn 89.5(5,2.1) Cl,Sn 177.31(9) C,C 110.2(4) C,Cl 102.1(3,2) C,Pt 116.2(3,2) Cl,Pt 108.0(1)	23
{η³-CH_2C(Me)CH_2}.{η²-styrene)Pt$SnCl_3$ (pale yellow)	tr P$\bar{1}$ 2	869.7(2) 937.3(2) 1101.5(2)	72.32(2) 89.76(2) 73.30(2)	PtC_5Sn $SnCl_3Pt$	η³C 216.3(9,29) η²C 218.1(9) 223.6(7) Cl 236.78(26,31)	Sn 253.93(7)	C,C 37.5(3,9)[f] 66.31-168.19(28) C,Sn 86.10 - 153.47(21) Cl,Cl 97.42(7,97) Cl,Pt 119.79(7,3.28)	24
[(η²-4,4'-Bu$^t_2$bpy)(Me)$_2$.PtSn(Me)$_2$Cl].BF_4 (colourless)	m $P2_1$ 2	1103.2(2) 1173.3(1) 1168.1(2)	 113.57(1) 	$Pt^{IV}N_2C_2Sn$ SnC_2ClPt	η²N 213.2(12,18) C_{Me} 208.5(17,8) C_{Me} 210.1(21,4) Cl 244.4(5)	Sn 254.1(2)	N,N 77.5(5)[c] C,C 90.7(5) N,C 97.1(7,1.4) 173.1(7,1) N,Sn 96.6(3,3.2) C,Sn 87.6(6,1.3) C,C 119.4(11) C,Cl 102.0(8,9) C,Pt 115.1(8,3.9) Cl,Pt 98.6(1)	25
[η²-4,4'-Bu$^t_2$bpy)(Me)$_2$.(I)PtSn(Me)$_3$]$_2$[Sn(Me)$_3$I][g] (yellow)	m $P2_1/m$ 2	1120.4(2) 1392.6(2) 2248.5(3)	 96.40(1) 	PtN_2C_2ISn SnC_3Pt PtN_2C_2ISn SnC_3Pt SnC_3I	ηN 214.0(18) C_{Me} 206.3(26) I 288.1(4) C_{Me} 217.6(36,0) 220.0(47) ηN 211.5(21) C_{Me} 204.8(24) I 285.9(4) C_{Me} 212.8(31,0) 228.9(56) C_{Me} 210.6(49) (x3) I 280.9(5)	Sn 254.7(5) Sn 256.7(4)	N,N 77.0(10)[c] C,C 88.1(14) N,C 97.5(9) I,Sn 179.6(1) C,C 107.9(18,2) C,Pt 110.9(17,5.9) N,N 74.7(11)[c] C,C 93.6(14) N,C 95.8(9) I,Sn 176.9(1) C,C 110.5(17,1.4) C,Pt 108.5(8,7) C,C 118.1(32,7.5) C,I 95.0(24,5.2)	26
[(η²-Me$_2$ann)$_2$(Cl)Pt$SnCl_3$].CH_2Cl_2	or $P2_12_12_1$ 4	1107.16(4) 1163.05(4) 2264.63(9)		$Pt^{IV}N_2C_2ClSn$ $SnCl_3Pt$	η²N 223.3(7) 234.8(6) ηC 201.0(7,1) Cl 241.0(2) Cl 211.4(9) 237.6(3,1)	Sn 254.89(5)	N,N 97.5(2) C,C 88.8(2) N,C 80.9(3,1.6)[c] 86.6, 176.8(3) N,Cl 94.76(18,3.4) C,Cl 88.8, 172.6(2) Cl,Cl 100.4(3,3.6) Cl,Pt 117.4(3,7.6)	27
(η³-C_4H_7)(OC)Pt$SnCl_3$ (colourless)	tr P$\bar{1}$ 2	891.2(2) 907.6(2) 726.3(1)	98.92(1) 105.80(2) 86.06(2)	PtC_4Sn $SnCl_3Pt$	ηC 215.3(7) 219.6(8,2) OC 187.8(1) Cl 235.8(2,0) 237.9(2)	Sn 254.96(7)	C,C 37.8(2,1)[f] 65.9, 169.1(3) 133.2, 169.1(3) C,Sn 95.4(2,4.8) 123.8, 157.0(2) Cl,Cl 96.96(6,3.66) Cl,Pt 19.26(5),5.03)	28
[(η⁴-pp3)PtHgCl]PF_6.CH_2Cl_2 (yellow) at 213(2)K	m $P2_1/n$ 4	1928.8(3) 1406.8(2) 1950.5(4)	 119.00(2) 	PtP_4Hg HgClPt	ηP 227.6(2,33) 234.3(2,9) Cl 237.7(2)	Hg 255.11(9)	P,Hg 93.63(6,7.35) 172.63(7) Cl,Pt 174.63(7)	29

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
[(η²-mpt)(η²-S_2CNMe_2). (η¹-CF_3COO)PtHg(η¹- CF_3COO)]. 0.5Me_2CO	tr $P\bar{1}$ 4	1419.1(12) 1493.7(12) 1948.8(15)	111.53(5) 102.65(4) 101.93(4)	PtS_2OCPHg	ηS 239.9(3,12) ηO 217.5(6) ηC 208.1(9) ηP 228.5(3)	Hg 255.35(3,12)	S,S 73.63(9) S,O 87.6(2,1) S,P 99.34(10) S,Hg 94.36(7) 167.78(7) O,Hg 94.4(2) C,Hg 87.3(3) P,Hg 92.34(7)	30
				HgOPt	ηO 213.7(7)		O,Pt 177.4(2)	
(η²-4,4'-Bu^t_2bpy)(Ph)(CNBu^t). (Bz)PtSn(η⁵-$B_{11}H_{11}$) (yellow)	m $P2_1/n$ 4	1128.3(2) 2528.3(3) 1710.9(3)	 93.18(2) 	PtC_3N_2Sn	C_{Ph} 206.4(8) C_{Bz} 214.5(8) NC 206.3(9) ηN 215.7(7,3)	Sn 255.4(1)	C,C 176.5(3) C,N 174.4(3) C,Sn 87.9(2,1.4) N,Sn 99.3(2) 174.0(2)	31
				SnB_5Pt	B not given		not given	
(η²-4,4'-Bu^t_2bpy)$(Me)_2$Pt. {μ-η²-SeC(CO_2Me)=C(CO_2Me)}. Sn$(Me)_2$[g] (yellow) at 150K	or $Pca2_1$ 8	3089.9(6) 1215.6(2) 1731.1(4)		$Pt^{IV}N_2C_2SeCSn$	ηN 214.4(6) 224.4(7) C_{Me} 207.7(9,15) Se 253.03(9)	Sn 255.78(7)	Se,Sn 88.60(3)	32
				SnC_3Pt	C_{Me} not given C not given		C,Pt 99.0(2)	
(η²-Me_2phen). (η²-$MeO_2CCH{=}CHCO_2Me$). ClPtHg(Me)	m $P2_1/c$ 4	1307.9(2) 1316.7(2) 1549.5(3)	 94.18(2) 	$Pt^{I}N_4ClHg$	ηN 218(2,2) ηC 206(2,1) Cl 259.0(6)	Hg 255.8(1)	N,N 76.3(6)[c] C,C 41.4(9)[f] N,Cl 91.1(4,1.8) N,Hg 87.3(4,1.8) C,Hg 92.8(6,5) Cl,H 173.9(8)	33
				HgCPt	C not given		C,Pt 173.9(8)	
$(Ph_3P)_2$ClPtHg. (η¹-camph-1-enyl)	or Pbca 8	2541(1) 3130(1) 1057.3(6)		$Pt^{II}P_2ClHg$	P_{Ph} 229(1,1) Cl 237(1)	Hg 256.1(2)	P,Cl 95.2(-,1.5) P,Hg 84.6(-,1.1)	34
				HgCPt	ηC 213(5)		C,Pt 172.1(3)	
(η²-dppc)ClPt$SnCl_3$[g]	m $P2_1/c$ 8	2201.9(1) 1479.4(1) 2221.0(1)	 119.366(5) 	PtP_2ClSn	ηP 228.5(6,2) Cl 236.1(7,2)	Sn 257.2(2)	P,P 86.9(2)[c] P,Cl 90.9(3) 177.2(3) P,Sn 97.2(1) 175.8(1) Cl,Sn 85.0(3)	35
				$SnCl_3Pt$	Cl 237(2,3)		Cl,Cl 98(1,6) Cl,Pt 118.7(8,3.6)	
				PtP_2ClSn	ηP 227.8(5,3) Cl 228.3(9)	Sn 256.2(2)	P,P 87.0(2) P,Cl 90.6(3) 176.9(3) P,Sn 97.3(1) 173.5(1) Cl,Sn 85.2(3)	
				$SnCl_3Pt$	Cl 232.6(8) 236.1(7,2)		Cl,Cl 96.7(3,3.4) Cl,Pt 120.3(2,2.8)	
$(Ph_3P)_2$HPtSn$(Ph)_3$ (pale yellow)	tr $P\bar{1}$ 2	1283.2(3) 1424.6(3) 1442.2(3)	73.46(4) 71.83(4) 66.71(3)	PtP_2HSn	P_{Ph} 229.8(1,8) H not given	Sn 256.4(1)	P,P 110.2(4) P,Sn 93.27(3) 155.75(3)	36
				SnC_3Pt	C_{Ph} 213.1(4,6)		C,C 104.4(1,7) C,Pt 114.7(1,9.0)	
$(Ph_3)_2(F_3C)$PtHg(CF_3)	m B2/b 8	2058.9(5) 4213.6(5) 979.21(9)	 98.84(2)	$Pt^{II}P_2CHg$	P_{Ph} 230.8(9) 233.4(8) F_3C 207(3)	Hg 256.9(2)	P,P 97.2(2) P,C 92.5(5) 169.3(5) P,Hg 88.0(1) 171.1(1) C,Hg 81.6(5)	37
				HgCPt	F_3C 209(4)		C,Pt 174(1)	
$(Me)_2$(η³-pz_3BH)PtSn$(Me)_3$ (yellow)	m $P2_1/n$ 4	786.5(2) 1308.07(9) 1939.6(3)	 91.60(2) 	$Pt^{IV}N_3C_2Sn$	η³N 223.2(7,5) C_{Me} 205(1,1)	Sn 257.27(8)	N,N 85.0(2,2.3) C,C 88.5(4) N,C 92.3(3,9) 176.4(4,1) N,Sn 95.9(2,5) 179.3(2) C,Sn 87.7(3,6)	38
				SnC_3Pt	C_{Me} 216(2)		C,C 104.7(7,4) C,Pt 113.9(4,1.7)	
[(η⁴-pp3)Pt$SnCl_3$]($SnCl_3$). $CHCl_3$ (yellow)	m $P2_1/c$ 4	1251.4(3) 4238.80(11) 1055.293)	 113.165(4) 	$Pt^{II}P_4Sn$	η⁴P 229.4(3) 237.4(3,8)	Sn 257.41(2)	P,P 84.10(2,35)[c] 118.97(2,1.31) P,Sn 95.91(6,1.21)	39
				$SnCl_3Pt$	Cl 235.6(4,14)		Cl,Cl 97.92(2,1.48) Cl,Pt 119.41(2,1.12)	
				$SnCl_3$	Cl 249.3(5,14)		Cl,Cl 93.35(2,1.2)	

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
$(Et_3P)_2(\eta^5\text{-}CB_{10}H_{11})PtHg(Ph)$ (yellow) at 173K	tg $P4_22_12_1$ 8	1849.1(4) 1745.0(3)		PtB_4CP_2Hg HgCPt	η[5]B 225.0(12,13) 232.4(11) η[5]C 235.0(9) P_{Et} 235.7(5,2) C_{Ph} 217(2)	Hg 258.50(5)	B,B 48.3(5,9)[f] B,C 43.3(4,1)[f] P,P 98.32(8) P,Hg 89.5(1,2.1) C,Pt 171.2(5)	40
$(\eta^2\text{-}Me_2phen)$. $(\eta^2\text{-}MeO_2CCH{=}CHCO_2Me)$. $(Cl)PtSn(Me)_2Cl$	tr $P\bar{1}$ 2	994.2(2) 1087.2(3) 1360.3(3)	79.00(2) 76.41(2) 63.67(2)	PtC_2N_2ClSn SnC_2ClPt	ηC 207.4(6,1) ηN 216.4(5,9) Cl 247.6(2) C_{Me} 213.8(8,4) Cl 243.8(2)	Sn 258.64(7)	C,C 41.0(2)[f] N,N 76.5(2)[c] Cl,Sn 177.53(4) C,C 114.4(4) C,Cl 95.7(3,2) C,Pt 119.7(3,5) Cl,Pt 103.52(5)	41
$(Et_3P)_2(\eta^1\text{-}Bu^tNC)PtSn(\eta^5\text{-}B_{11}H_{11})$ (pale yellow)	m $P2_1/n$ 4	1069.8(2) 1717.0(2) 1787.7(3)	 107.26(2)	PtP_2CSn SnB_5Pt	P_{Et} 233.7(2,4) ηC 191.3(10) ηB not given	Sn 259.0(1)	P,P 175.0(1) P,C 91.3(3,8) P,Sn 89.1(1,1.9) C,Sn 171.7(3) not given	42
$(PPh_3)_2(Cl)PtSnCl_3$ (yellow)	m $P2_1/n$ 4	1289.5(3) 1684.4(3) 1662.0(3)	 102.38(1)	PtP_2ClSn	P_{Ph} 225.6(2) 231.7(2) Cl 233.3(2)	Sn 259.0(1)	P,P 97.2(1) P,Cl 91.9(1) 170.7(1) P,Sn 93.0(1) 168.3(1) Cl,Sn 78.0(1) Cl,Cl 97.9(1,2.8) Cl,Pt 119.3(1,7.9)	43
$(\eta^4\text{-}C_4Me_4)Cl_2PtSb(Ph)_3$ (pale yellow)	m $P2_1/n$ 4	830.3(1) 1737.8(2) 1764.0(2)	 90.86(1)	$Pt^{II}C_4Cl_2Sb$ SbC_3Pt	ηC 210.6(4,1) 218.8(5,8) Cl 245.3(1,5) C_{Ph} 211.8(4) 213.2(4,0)	Sb 259.11(4)	C,Cl 92.74- 148.96(13) Cl,Cl 95.33(14) C,Sb 111.8(1,2.4) 149.1(1,2.4) Cl,Sb 86.95(3,2.0) C,C 101.4(2,1.6) C,Pt 116.6(1,4.0)	44
$[(Ph_3P)(Bu^tNC)\{\eta^1\text{-}C(Ph).NHBu^t\}PtSn(\eta^5\text{-}B_{11}H_{11})]$. $2CH_2Cl_2$ (yellow)	tr $P\bar{1}$ 2	1037.3(3) 1312.0(2) 1823.3(3)	73.57(2) 80.90(2) 78.08(2)	PtC_2PSn SnB_5Pt	C_{LN} 196.7(7) ηC 202.1(7) P_{Ph} 232.4(2) ηB 231.2(10,15)	Sn 259.5(1)	C,C 173.1(3) C,P 92.7(3,1.7) C,Sn 87.4(2,1.0) P,Sn 177.3(1) not given	45
$(\eta^2\text{-}dppe)\{\eta^1\text{-}C(Ph)NHBu^t\}$. $PtSn(\eta^5\text{-}B_{11}H_{11})].2CH_2Cl_2$. MeOH (yellow)	m $P2_1/c$ 4	1185.7(2) 1946.3(2) 2252.1(3)	 91.86(2)	PtP_2CSn SnB_5Pt	η[2]P 230.3(2,3) ηC 204.7(8) ηB 231.0(11,24)	Sn 260.1(1)	P,P 84.5(1)[c] P,C 94.9(2) 176.3(2) P,Sn 92.5(1) 176.4(1) C,Sn 88.1(2) not given	45
$(Ph_3)_2(H)PtSnCl_3$ (yellow)	m C2/c 8	3134.5(5) 1271.6(3) 1813.5(3)	 96.5(2)	PtP_2HSn $SnCl_3Pt$	P_{Ph} 230.1(4,2) H not given Cl 228.3(5) 237.0(6,3)	Sn 260.1(1)	P,P 161.3(1) P,Sn 98.9(1,4) Cl,Cl 96.8(2,3.8) Cl,Pt 120.4(1,4.9)	46
$(\eta^2\text{-}dcpe)(\eta^1\text{-}CH_2SiMe_3)$. $PtIn(\eta^1\text{-}CH_2SiMe_3)_2$ (colourless)	not given			PtP_2CIn InC_2Pt	ηP 225.1(1) 229.5(1) ηC 214.7(3) ηC not given	In 260.12(2)	P,P 86.9(3)[c] P,C 176.36(8) P,In 173.67(2) P,C 84.74(8)	47
$(Et_3P)_2(Cl)PtSb(\eta^1\text{-}C_{10}H_{10}O)_2$	m $P2_1/n$ 4	1863.4(1) 1012.79(5) 1882.86(11)	 91.568(3)	PtP_2ClSb SbC_2Pt	P_{Et} 233.30(14) 234.18(13) Cl 241.01(13) ηC 227.6(5,19)	Sb 260.42(4)	Cl,Sb 173.92(3) C,C 96.46(18) C,Pt 107.41(14,2.58)	48
$[(\eta^2\text{-}bpy)(Me)_2PtCd$. $(\eta^4\text{-}cyclen)](ClO_4)_2$. Me_2CO (yellow)	m C2 4	2096.6(2) 1131.4(1) 1658.2(2)	 120.944(2)	$Pt^{II}N_2C_2Cd$ $Cd^{II}N_4Pt$	ηN 212.5(10,5) C_{Me} 205(2,1) ηN 237(3,2)	Cd 261.01(8)	N,C 98.8(9) 174(1) N,N 117(1) N,Pt 118.1(7,7.8)	49
$(\eta^2\text{-}dppp)(I)PtSnCl_3$[g] (yellow)	m $P2_1$ 4	1548.8(2) 1499.9(2) 1630.3(2)	 98.67(1)	PtP_2ISn $SnCl_3Pt$ PtP_2ISn $SnCl_3$	ηP 224.8(4) 2303(5) I 265.65(13) not given ηP 225.3(4) 229.7(4) I 264.15(13) not given	Sn 261.13(13) Sn 261.54(14)	P,P 95.7(2)[e] P,I 90.71(13) 172.48(13) P,Sn 90.64(12) 173.66(13) I,Sn 82.96(4) not given P,P 91.0(2)[e] P,I 91.00(11) 170.84(14) P,Sn 91.95(12) 174.67(13) I,Sn 86.73(4) not given	50

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
$[(\eta^3\text{-triphos})PtSn(\eta^5\text{-}B_{11}H_{11})]$. 2dmso (yellow) at 170K	tr $P\bar{1}$ 2	1074.2(2) 1373.9(2) 1762.3(3)	91.70(2) 106.98(2) 107.7(2)	PtP_3Sn SnB_5Pt	ηP 227.0(3) 231.0(3,5) ηB not given	Sn 262.6(1)	P,P 84.73(11,5)[e] 167.35(11) P,Sn 95.4(1,1.7) 177.7(1) not given	42
$(Ph_3P)_2(\eta^1\text{-}Me_2NB)PtSn(Me)_3$ (colourless)	tr $P\bar{1}$ 2	1170.9(2) 1205.0(3) 1812.4(4)	102.305(7) 96.281(8) 110.740(8)	$Pt^{II}P_2BSn$ SnC_3Pt	P_{Ph} 230.3(1) 236.9(1) ηB 213.6(4) not given	Sn 262.89(6)	P,P 102.15(4) P,B 87.6(1) 170.3(1) P,Sn 95.92(3) 161.63(2) B,Sn 74.4(1) not given	16
$[(NC)_5PtTl(dmso)_3(\eta^3\text{-phen})]$. dmso	m $P2_1/n$ 4	1092.06(2) 1717.43(3(3) 1845.41(3)	 98.8160(6)	$Pt^{IV}C_5Tl$ $Te^{I}O_3N_2Pt$	NC 200.9(6,2) 203.0(6) 205.4(6,1) O 247.1(5,24) ηN 237.8(4,56)	Tl 262.96(3)	C,C 177.4(2) C,Tl 177.58(18) N,Pt 176.21(12)	51
$(Ph_3P)_2Pt(\eta^1\text{-dpb})Sn(Me)_3$ (colourless)	m $P2_1/n$ 4	1040.67(2) 2333.06(4) 1956.94(1)	 92.262(1)	PtP_2BSn SnC_3Pt	P_{Ph} 230.1(1) 237.6(1) ηB 208.5(6) not given	Sn 263.39(4)	P,P 99.74(5) P,B 90.5(2) 165.7(2) P,Sn 93.50(3) 164.62(5) B,Sn 77.9(2) not given	16
$(Et_3P)_2(\eta^1\text{-COPh})PtSnCl_3$ (yellow)	or $P2_12_12_1$ 4	1026.6(3) 1547.6(2) 1744.0(2)		PtP_2CSn $SnCl_3Pt$	P_{Et} 232.7(4,3) ηC 205(1) Cl 238.3(7,15)	Sn 263.4(1)	P,P 170.7(6) P,C 88.6(4,3) P,Sn 91.9(1,2) C,Sn 173.0(3) Cl,Cl 96.5(2,1.6) Cl,Pt 112.3(1) 124.5(1,6)	52
$[(NC)_5PtTl(\eta^2\text{-phen})_2]$.3(dmso)	m $P2_1/c$ 4	1464.40(1) 2472.40(3) 1167.00(2)	 106.6090(4)	$Pt^{IV}C_5Tl$ $Te^{I}N_4Pt$	NC 199.6(9,6) 202.5(11,4) ηN 229.1(10) 244.2(7,14) 252.4(10)	Tl 263.75(5)	C,C 90.8(5) 177.6(4) C,Tl 178.3(4) N,Pt 103.3(4,2) 118.2(2) 158.6(2)	51
$[(\eta^2\text{-phpy})_2PtCd(\eta^4\text{-cyclen})]$. $(ClO_4)_2.Me_2CO$ (yellow)	m $P2_1/n$ 4	1335.2(1) 1403.5(1) 2026.9(2)	 106.599(2)	$Pt^{II}N_2C_2Cd$ $Cd^{II}N_4Pt$	ηN 213.4(8,6) ηC 202.5(10,25) ηN 233(1,3)	Cd 263.89(8)	N,C 78.7(3,2)[c] N,Pt 122.3(3,4.4)	49
$[(Ph_3P)_2(Me)PtSb(\eta^3\text{-ad})]$. $SbF_6.0.5C_6H_8SiO$ (dark red)	m $P2_1/c$ 4	1246.6(3) 1752.9(4) 2749.3(5)	 92.64(2)	PtP_2CSb SbO_2NPt	P_{Ph} 230.9(4,2) C_M 208.0(2) ηO 217.7(9,16) ηN 210.3(12)	Sb 264.1(1)	C,P 86.2(4,2.6) P,Sb 93.8(1,4.0) O,O 146.2(4) O,N 73.3(4,1)[c] N,Pt 118.5(3)	53
$[(\eta^2\text{-}Me_2phen)(Cl)PtPb(\mu\text{-}\eta^2\text{-}Me_2mal)Pb(Ph)_2Cl].3CHCl_3$	tr $P\bar{1}$ 2	1145.8(5) 1167.8(2) 1808.8(5)	74.90(1) 75.83(2) 79.66(2)	PtN_2C_2ClPb PbC_2OClPt	ηN 217.0(7,10) C 210(2,1) Cl 244.7(6) C_{Ph} 220(1,1) O 266(1) Cl 261.8(6)	Pb 264.2(1)	N,N 75.7(2)[c] Cl,Pb 178.7(1) C,C 110.0(6) O,C 174.7(3) C,Pt 123.5(4,3.9) Cl,Pt 101.2(1) P,Pt 81.0(3)	54
$(NMeBu_3)[(Ph_3P)(Ph)$. $PtSn(\eta^5\text{-}B_{11}H_{11})$	m $P2_1/c$ 4	2562.3(4) 1053.3(1) 2178.6(3)	 101.76(2)	PtP_2CSn SnB_5Pt	P_{Ph} 230.2(1,4) C_{Ph} 206.2(5) ηB not given	Sn 265.1(1)	P,P 176.05(4) P,C 89.17(13,70) P,Sn 91.19(3,6) C,Sn 167.98(13) not given	55
$(Ph_3P)_2(Ph)PtPb(Ph)_3$ (pale yellow)	m $P2_1/c$ 4	2250.1 1050.2 2412.0	 113.43	PtP_2CPb PbC_3Pt	P_{Ph} 231.9(20,12) C_{Ph} 205.5(30) C_{Ph} 227.0(30,22)	Pb 269.8(10)	P,P 101.6(2.0) P,C 87.5; 168.6 P,Pb 90.5; 165.8 C,Pb 81.2 C,C 98.4(2.0,3.1) C,Pt 118.7(2.0,9.1)	56
$[(H_3N)_2Pt(\mu\text{-}\eta^2\text{-1-mec})_2Hg]$. $(NO_3)_2.2H_2O$ (colourless)	or Pbca 8	1342.3(1) 2350.6(5) 1373.8(3)		$Pt^{II}N_4Hg$ $Hg^{II}N_2Pt$	H_3N 204.1(12,15) ηN 202.9(12,3) ηN 207.3(10,7)	Hg 274.98(6)	N,N 90.2(6,1.4) N,Hg 87.0(4,7.0) N,N 165.9(4) N,Pt 83.2(3) 165.9(4)	57
$[(H_3N)_2Pt(\mu\text{-}\eta^2\text{-meu})_2Zn(H_2O)_3]$. $SO_4.3H_2O$ (yellow)	m $P2_1/c$ 4	1053.4(1) 1793.3(2) 1149.0(1)	 94.61(1)	$Pt^{II}N_4Zn$ $Zn^{II}O_5Pt$	H_3N 204.3(7,2) μN_L 204.5(6,8) H_2O 208.1(8,37) μO_L 206.3(6,27)	Zn 276.0(1)	N,N 90.0(3,2.2) 176.8(3,5) N,Zn 91.3(2,8.6) O,O 91.8(3,5.6) 171.4(3,8) O,Pt 86.4(2,6.2) 169.9(2)	58

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
$[(MeNH_2)_2Pt(\mu\text{-}\eta^2{:}\eta^2\text{-}1,5\text{-}dmec)_2Hg](NO_3)_2.0.5H_2O$ (colourless)	m $P2_1/n$ 4	861.4(3) 2061.0(6) 1398.4(3)	 97.67(2)	$Pt^{II}N_4Hg$ $Hg^{II}N_2Pt$	ηN 204.7(6,6) ηN 203.7(5,18) ηN 203.5(6,2)	Hg 276.5(1)	N,N 90.2(2,2.6) 173.3(2,6) N,Hg 89.7(2,6.7) N,N 164.1(2) N,Pt 82.1(2,7)	59
$[(MeNH_2)_2Pt(\mu\text{-}\eta^2{:}\eta^2\text{-}1\text{-}mec)_2Hg].(NO_3)_2$ (colourless)	tr $P\bar{1}$ 2	1015.7(4) 1049.4(4) 1145.2(4)	101.33(2) 102.44(2) 104.65(2)	$Pt^{II}N_4Hg$ $Hg^{II}N_2Pt$	N 207.0(8,17) ηN 203.5(8,1) ηN 203.5(10,5)	Hg 278.5(1)	N,N 90.3(3,1.4) 172.1(4,9) N,Hg 89.6(2,5.8) N,N 163.2(3) N,Pt 81.9(3,2)	59
$[(\eta^3\text{-}damp)Pt(\mu\text{-}\eta^2\text{-}tcap)HgClBr].CH_2Cl_2$ (orange)	m $P2_1/c$ 4	919.2(5) 1201.6(5) 2689.5(4)	 94.30(3)	$Pt^{II}N_3CHg$ HgNClBrPt	ηN 209(1,1) ηC 191(1) μN_L 215.5(9) μN_L 216(1) Cl 246.5(3) Br 250.9(3)	Hg 283.31(7)	N,N 98.3(4,1) 159.5(4) N,C 82.1(4,9)[c] 177.0(4) N,Cl 126.3(3) N,Br 117.0(3) Cl,Br 106.8(1)	60
$\{Cl_2Pt\{\mu\text{-}\eta^2\text{-}Ph_2PC_6H_4\}_2Hg].2CH_2Cl_2$ (pale yellow)	or Pbca 4	1980.5(3) 853.2(4) 2307.6(2)		$PtCl_2P_2Hg$ HgC_2Pt	Cl 231(1,1) P 230.6(5,6) C 237(1,1)	Hg 283.39(7)	Cl,Cl 178.3(3) P,P 172.0(2) Cl,P 90.0(3,4.1) Cl,Hg 89.2(2,3.6) P,Hg 86.0(1,1.7) C,C 174.0(3)	61
$[(MeNH_2)_2Pt(\mu\text{-}\eta^2{:}\eta^2\text{-}1\text{-}mec)_2Hg].Cl.NO_3$ (colourless)	m C2/m 4	1387.6(4) 1625.4(3) 1035.8(3)	 112.02(1)	$Pt^{II}N_4Hg$ $Hg^{II}N_2Pt$	N 203(1,0) ηN 203.5(6) ηN 211.7(6)	Hg 283.5(1)	N,N 90.2(1,7) 174.7(3,1.1) N,Hg 90.6(3,2.7) N,N 156.2(3) N,Pt 78.1(2)	59
$\{(Ph_2(py)P)_3PtTl](ac)$ (orange) at 140K	tr $P\bar{1}$ 2	1114.7(1) 1143.6(1) 2067.4(2)	101.015(2) 95.79(2) 97.056(2)	$Pt^0P_3Tl^I$ TlPt	P 227.3(1,3) 228.3(1)	Tl 286.53(4)	P,P 120.00(5,5.3) not given	62
$[(Ph_3P)_3PtTl](NO_3)$ (orange) at 140K	tr $P\bar{1}$ 2	1445.4(2) 1732.4(3) 1975.4(2)	106.09(1) 99.42(1) 102.09(1)	$Pt^0P_3Tl^I$ TlPt	P 228.1(2,1) 229.7(2)	Tl 288.8(5)	P,P 120.00(7,10.1) not given	63
$(NC)_2Pt(\mu\text{-}\eta^2\text{-}\eta^6\text{-}crownP_2)Tl].(NO_3.1.5H_2O.0.5CH_2Cl_2$[g] (colourless) at 130K	m $P2_1/c$ 8	2147.6(7) 1427.4(4) 3266.0(9)	 104.36(2)	PtC_2 TlO_4N_2 PtC_2P_2 TlO_4N_2	NC 201(3,2) ηP 233.6(8,7) ηO 276(2,1) ηN 308(2,7) NC 199(3,1) ηP 232.3(11,11) ηO 283(2,8) ηN 302(2,4)	Tl 291.1(2) Tl 295.8(2)	C,C 174.4(14) P,P 171.0(3) C,P 89.8(8,5.6) O,O 60.1(14,6)[d] O,N 63.5(15,2.4)[d] C,C 175.9(17) P,P 172.0(3) C,P 89.9(11,10.6) O,O 63.0(17,4)[d] O,N 62.2(17,2.7)[d]	63
$[Pt(\mu\text{-}\eta^2\text{-}mbo)_4CaCl].[(\eta^1\text{-}hmpa)_3Ca(\mu\text{-}Cl)_3.Ca(\eta^1\text{-}hmpa)_3].2tol$ (yellow)	m $P2_1/c$ 4	1975.0(4) 2422.3(4) 2437.9(5)	 101.13(2)	$Pt^{II}S_4$ $Ca^{II}N_4Cl$ $Ca^{II}O_3Cl_3$ (dimer)	S 232(2) N 246(2) Cl not given ηO_L 227(2) μCl 280(1)	Ca 295.0(5)	S,S 90 not given not given	64
$(Ph_3P)(\eta^1\text{-}C_6F_5)_2Pt(\mu\text{-}\eta^2\text{-}ac)Tl$ (colourless)	tr $P\bar{1}$ 2	913.6(1) 986.4(2) 1814.8(2)	95.08(1) 101.89(1) 102.00(1)	PtC_2OPTl TlOPt	ηC 201.3(10) 206.7(12) μO_L 210.7(7) P_{Ph} 232.6(3) μO_L 248.9(8)	Tl 299.4(1)	C,C 87.2(5) O,P 90.9(2) C,O 88.2(4) 171.0(4) C,P 92.5(4) 172.0(4) O,Pt 74.6(2)[c]	65
$(\eta^2\text{-}Ph_2PC_6H_4)Pt(\mu\text{-}\eta^2\text{-}Ph_2PC_6H_4)_2.HgCl$ (white) at 193K	m $P2_1/c$ 4	1315.0(3) 1291.2(6) 2672.4(2)	 94.99(1)	PtC_2P_2 HgCCl	C 205.8(8,5) P 233.1(2,2) C 211.1(2) Cl 254.6(2) P 241.4(2)	Hg 313.35(5)	C,C 92.9(3) P,P 104.87(8) C,P 67.9(2)[d] 94.7(2) 164.4(2,4.0) C,Cl 102.9(2) C,P 158.6(2) Cl,P 97.64(7)	61
$(\eta^2\text{-}dppe)Pt(\mu\text{-}\eta^2\text{-}C_5H_4N)\{\mu\text{-}\eta^2\text{-}C(OEt)(NHC_6H_4OMe\text{-}4\}ZnCl_2$	or $Pna2_1$ 4	2420.6(3) 1426.9(3) 1287.5(3)		PtC_2P_2 ZnN_2Cl_2	μC_L 204.0(9,5) ηP 230.1(3,4) μN_L 203.9(8,18) Cl 225.0(3,26)	Zn 323.8(1)	C,C 89.6(4) P,P 82.8(1)[c] C,P 93.2(3,2.0) 170.8(3,2.3) N,N 98.2(3) Cl,Cl 110.8(1) N,Cl 111.7(2,6.6)	66

Continued **Table 1.** Heterobinuclear platinum compounds with M = main group metal atom[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm]	L – M – L [°]	Ref.
$Cl(Me)Pt(\mu\text{-}\eta^2\text{-dppm})_2HgCl_2$ (white)	or $P2_12_12_1$ 4	1001.1(1) 1657.2(1) 2824.3(1)		$Pt^{II}P_2CCl$ $Hg^{II}Cl_2P_2$	P 227.8(4,9) C_{Me} 219.0(12) Cl 241.6(4) Cl 262.3(5,92) P 249.7(4,10)	Hg 330.2(1)	P,P 176.2(2) C,Cl 173.2(4) P,C 91.7(4,1.8) P,Cl 88.2(2,8) Cl,Cl 90.9(2) P,P 135.9(1) Cl,P 103.5(1,8.0)	67
$[(NC)_2Pt(\mu\text{-}\eta^2\text{:}\eta^6\text{-crownP}_2)$. $Pb(\eta^2\text{-ac})](ac).1.5H_2O$. $MeOH.2.5CHCl_3$ (colourless) at 130K	m $P2_1/n$ 4	1348.3(4) 24.125(10) 1621.2(4)	 90.06(2)	PtC_2P_2 PbO_6N_2	NC 196.5(20,15) ηP 232.0(6,10) ηO_{ac} 252(1,1) η^6O_L 263(1,10) η^6N_L 282(2,1)	Pb 331.3(2)	C,C 175.4(8) P,P 170.4(2) C,P 90.2(6,5.8) O,O 52.1(5)[3] 62.0(5,7)[5] O,N 63.9(5,1.2)[5]	63
$(NBu_4)_2[(\eta^1\text{-}C_6F_5)_2Pt$. $(\mu\text{-}\eta^2\text{:}\eta^4\text{-}C{=}CSiMe_3)HgBr_2]$. CH_2Cl_2 (white)	m $P2_1/c$ 4	1825.6(3) 1875.7(4) 2118.4(4)	 99.05(1)	PtC_4 $Hg^{II}C_4Br_2$	ηC 208(3,2) μC 196.5(30,15) ηC 244(2,3) ηMC 261(2,4) Br 258.0(3,8)	Hg 362.7(5) C 104.2(9,8)	μC,μC 88.0(9) μC,C 92.1(9,1.8) 178.1(9) μC,μC 63.1(8) μC,C 27.3(7)[f] Br,Br 113.01(10) μC,Br 119.0(5,3.6) C,Br 107.3(6,3.9)	68
$(PMe_2Ph)_2Pt(\mu\text{-}Cl)_2HgCl_2$ (white)	m $P2_1/c$ 4	909.2(3) 1043.8(4) 2428.6(8)	 105.12(2)	$Pt^{II}P_2Cl_2$ $Hg^{II}Cl_4$	P_{Ph} 225.5(7,2) μCl 237.1(8,11) Cl 231.7(9,5) μCl 284.3(8,9)	Hg 403.7(2)	P,P 94.5(3) Cl,Cl 87.1(3) P,Cl 89.3(3,1.2) 175.1(3,3) Cl,Cl 156.9(3) μCl,μCl 70.2(3) Cl,μCl 99.3(3,3.7)	69
$(PMe_2Ph)Pt\{\mu\text{-}\eta^3\text{:}\eta^3\text{-}$ $S(O)P(OPr^i)_2\}_2ZnCl$ (yellow)	m $P2_1/n$ 4	1270.2(3) 2093.6(3) 1587.6(3)	 91.64(2)	PtS_3P ZnO_3Cl	S 233.6(2,3) 240.2(2) P 224.1(2) O 194.0(5) 196.5(5,2) Cl 219.1(2)	Zn 439	S,S 94.0(1) 173.3(1) S,P 94.3(1) 165.9(1) O,O 99.7(2) 111.1(2,4) O,Cl 111.5(2,1.5)	70
$(PMe_2Ph)_2Pt(\mu\text{-}\eta^2\text{-}S(O)$. $P(OPr^i)_2\}_2ZnCl_2$ (pale yellow)	m $P2_1/n$ 4	1174.8(3) 2314.6(7) 1571.4(4)	 104.91(2)	PtS_2P_2 ZnO_2Cl_2	μS_L 239.6(1,7) P 227.0(2,12) μO_L 195.4(4,12) Cl 222.8(2,4)	Zn 439	S,S 87.1(1) P,P 94.2(1) O,O 101.7(2) Cl,Cl 119.1(1) O,Cl 107.8(2,2.7)	71
$(H_3N)Pt(\mu\text{-}\eta^2\text{-mquaH})_2$. $(\mu\text{-}\eta^2\text{-mcyt})Na(H_2O)_2(OClO_3)]$. $(ClO)_2.0.5H_2O$ (colourless)	tr $P\bar{1}$ 2	1099.0(2) 1227.3(2) 1374.3(3)	89.84(3) 70.51(3) 88.28(3)	$Pt^{II}N_4$ Na^IO_6	H_3N 202.0(7) ηN 201.5(7,1) 203.9(8) ηO 241(1,17) H_2O 239(2,1) O_3ClO 288(2)		N,N not given not given	72
$[(H_3N)_2Pt(\mu\text{-}\eta^2\text{-myct})_2$. $K(F_2PF_4)_2]PF_6.H_2O$ (colourless)	m C2/c 8	822.9(2) 2203.6(4) 1538.5(3)	 90.48(3)	$Pt^{II}N_4$ $K^IF_4O_2$	H_3N 203.5(4) ηN 205.1(4) F 284(4,1) ηO 268.9(4)		N,N 90.5(2) 177.1(2,2.5)	72
$(PH_3P)_2Pt\{\mu\text{-}\eta^2\text{:}\eta^1\text{-}S(C)$. $SMe\}Sn(Ph)_3$ (pale yellow	tr $P\bar{1}$ 2	1190.76(33) 1245.11(37) 1846.47(36)	95.22(2) 100.49(2) 114.92(2)	PtP_2CS SnC_4	P_{Ph} 226.1(4) 232.9(5) μC 212.2(17) S 230.2(5) C_{Ph} 215(2,1) μC 217(2)	 C 122.2(8)	P,P 100.3(2) C,S 48.5(5)[f] P,C 108.2(5) P,S 103.0(2) C,μC 111.1(7,6.0)	73
$[(Et_3P)_2(Cl)Pt(\mu\text{-}\eta^2\text{-}$ $P_2C_2Bu^t{}_2)Sb]$	or Pnma 4	1808.8(2) 1331.3(2) 1289.6(3)		PtP_3Cl SbCP	P_{Et} 232.46(12) μP 225.3(2) Cl 234.9(2) C 198.7(7) μP 232.7(2)		P,P 168.76(6) P,μP 94.04(3) P,Cl 85.73(3) μP,Cl 176.52(6) C,P 85.9(2)	74
$Pt(\mu\text{-}\eta^2\text{-}Ph_2PthqH)_2ZnBr_2$ (yellow)	m $P2_1/c$ 4	1303.0(9) 3070.1(13) 1246.0(9)	 113.81(3)	PtO_2P_2 ZnO_2Br_2	μO 207.0(5,10) P 221.8(3,1) μO 201.3(6,2) Br 234.5(2,4)		O,O 76.2(2) P,P 100.0(1) O,P 92.0(2,3) 167.8(2,3) O,O 78.8(2) Br,Br 116.0(1) O,Br 106.9(2,1.3) 121.9(2,1.4)	75

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]Four membered metallocyclic ring. [e]Six membered metallocyclic ring [f]Three membered metallocyclic ring [g]Two crystallographically independent molecules present.

Table 2. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Cu, Ag or Au)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$[MeNH_2)_2Pt(\mu-\eta^2-1-mec)_2.Cu(\eta^1-9-Etgh)(H_2O)].(ClO_4)(NO_3).H_2O$ (green)	m $P2_1/c$ 4	1193.4(3) 1057.2(4) 24.934(7)	 90.80(2)	$Pt^{II}N_4Cu$ $Cu^{II}N_3Pt$	N^b 206.7(10,2) μηN 202.5(9,5) N 197.7(10) μηN 189.5(10,1)	Cu 250.1(2)	N,N^b 90.0(4,1.1) 177.9(4,1.3) N,Cu 89.3(3,3.1) N,N 93.8(4,1.1) 172.5(4) N,Pt 86.4(2,8) 167.1(3)	77
$[(MeNH_2)_2Pt(\mu-\eta^2-1-mec)_2.Cu(\eta^2-1-mec)].(ClO_4).0.5\ H_2O$	m $P2_1/a$ 4	752.3(3) 3055.7(14) 1317.7(62)	 99.71(3)	$Pt^{II}N_4Cu$ $Cu^{II}N_3Pt$	N 206.5(10,15) μηN 199.5(10,5) N 199(2) μηN 188.5(20,25)	Cu 253.0(2)	N,N 90.0(5,5) 176.2(5,1) N,Cu 87.6(4,3.1) 177.6(1) N,N 95.2(6,1.1) 169.6(7) N,Pt 85.1(5)	77
$[(MeNH_2)_2Pt(\mu-\eta^2-1-mec)_2.Cu(OH)].PF_6.2H_2O$	tr $P\bar{1}$ 2	777.6(4) 1192.9(11) 1383.7(8)	92.68(6) 100.50(5) 93.15(6)	$Pt^{II}N_4Cu$ $Cu^{II}N_2OPt$	N 206(2,0) μηN 203(2,1) μηN 192(2,1) HO 192(2)	Cu 254.1(4)	N,N 90.0(8,1.8) 176.7(8,1.1) N,Cu 91.2(6,2.6) N,N 168.0(8) N,O 96.0(8,1.8) N,Pt 84.3(6,2) O,Pt 170.2(6)	77
$[(MeNH_2)_2Pt(\mu-\eta^2-1-mec)_2.Cu(NH_3)](ClO_4)_2.1.5\ H_2O$	or $P2_12_12_1$ 4	1214.8(13) 1429.6(12) 1714.0(10)		$Pt^{II}N_4Cu$ $Cu^{II}N_3OPt$	N 205.5(15,5) μηN 204(1,1) N 201(2) μηN 191(2,3) H_2O 233(1)	Cu 255.6(2)	N,N 90.0(5,2.4) 175.7(5,1) N,N 94.4(6,7) 168.8(6) N,O 93.3(6,6) N,Pt 164.3(5) O,Pt 101.9(3)	77
$(Et_3P)_2Pt(\mu-\eta^5:\eta^4-CB_{10}H_{11}).Cu(PPh_3)$ (pale yellow) at 173K	m $P2_1/n$ 4	1248.0(2) 1924.4(3) 1604.6(4)	 91.682(11)	PtB_4CP_2Cu CuH_2B_2PPt	ηB 226.1(3,10) μηB 227.5(4,10) μηC 244.9(3,9) P_{Et} 231.78(8,9) ηH 205(4,5) ημB 226.3(4,5) P_{Ph} 219.23(9)	Cu 260.58(5)	B,B 48.0(1,1.0) 78.2(1,3.1) P,P 99.35(3) P,Cu 99.51(2,5.7) H,H 98(2) B,B 47.23(14) P,Pt 148.81(3)	40
$(Et_3P)_2(\eta^5-CB_{16}H_{11}).PtAu(PPh_3)$ (pale yellow) at173K	or Pnma 4	1859.7(2) 1559.1(3) 1293.2(4)		PtB_4CP_2Au AuPPt	η^5B 224.9(6,11) ηC 238.7(7) P_{Et} 234.87(14) P not given	Au 261.12(7)	B,B 48.1(3,1.0)[c] 78.8(3,2.0) P,P 98.99(8) P,Au 88.27(4) P,Pt 167.51(5)	40
$[(Ph_3P)_3PtAu(PPh_3)]BF_4.thf$ (yellow)	m $P2_1/c$ 4	2042.6(6) 1349.8(1) 2470.3(9)	 97.166(15)	PtP_3Au AuPPt	P_{Ph} 228.9(2,19) 234.8(2) P_{Ph} 228.8(2)	Au 261.58(7)	P,P 104.76(8,4.79) 149.79(8) P,Au 76.13(6,39) 168.26(6) P,Pt 171.13(6)	78
$(C_6F_5)_3(SC_4H_8)PtAg(PPh_3)$ (white)	m $P2_1/n$ 4	1400.6(2) 1744.1(3) 1740.7(2)	 110.74(1)	$Pt^{II}C_3SAg$ Ag^IPPt	C 200.2(11) 208.2(12,14) S 232.8(3) P_{Ph} 235.8(3)	Ag 263.7(1)	C,C 87.4(5,7) 173.2(5) C,S 92.4(3,2.0) 173.2(5) C,Ag 87.9(3) 97.9(3,7) S,Ag 88.00(8) P,Pt 174.31(9)	79
$(NBu_4)[(C_6F_5)_4PtAg(tht)].0.5tol$ (white)	tr $P\bar{1}$ 2	1167.0(8) 1223.5(5) 2092(10)	103.87(3) 91.64(4) 116.95(2)	$Pt^{II}C_4Ag$ Ag^ISPt	C 204.3(18,11) 209.2(18) S 240.1(6)	Ag 264.1(1)	C,C 89.9(7,2.8) C,Ag 92.6(5,1.7) S,Pt 168.6(2)	80
$(C_6F_5)_2(C_6Cl_5)(tht).PtAg(PPh_3)$ (white)	m $P2_1/n$ 4	1435.0(3) 1775.0(5) 1773.3(4)	 110.35(2)	$Pt^{II}C_3SAg$ Ag^IPPt	C 205.3(22,37) 212.0(21) S 234.5(7) P_{Ph} 263.6(8)	Ag 265.0(2)	C,C 87.5(9,1.2) C,S 92.2(6,3.0) 172.8(7) C,Ag 95.0(6,9.6) P,Pt 173.0(2)	80
$(NBu_4)[(C_6F_5)_2(C_6Cl_5)_2.PtAg(tht)]$ (white)	tr $P\bar{1}$ 2	1197.8(2) 1239.8(3) 1999.6(4)	94.812(11) 91.950(10) 116.016(10)	$Pt^{II}C_4Ag$ Ag^ISPt	C 207.2(23,34) 209.2(22,32) S 242.4(8)	Ag 269.2(2)	C,C 90.0(9,2.7) C,Ag 91.3(6,6.9) S,Pt 169.3(2)	80
$[(PEt_3)_2(C_6F_5)Pt(\mu-H).Au(PPh_3)].CF_3SO_3$ (white)	m $P2_1/c$ 4	2360.9(5) 972.5(4) 1968.3(5)	 72.91(2)	$Pt^{II}P_2CHAu$ Au^IHPPt	P 231.5(4,2) C 207.1(1) μH 174(8) μH 172(9) P 226.4(4)	Au 271.4(1) H 103(4)	P,P 173.0(2) C,H 170(4) P,C 91.6(4,6) P,H 88(3,0) P,Au 90.1(1,2.1) C,Au 151.51(9) H,Au 38(2) H,P 172(3) H,Pt 38(2) P,Pt 146.38(3)	81

Continued Table 2. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Cu, Ag or Au)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$[(PEt_3)_2(C_6Cl_5)Pt(\mu\text{-}H).Ag(H_2O)].CF_3SO_3$ (colourless) (by Neutron Diffraction) at 24(1)K	tr $P\bar{1}$ 2 tr $P\bar{1}$ 2	873.9(4) 1208.0(18) 1587.0(11) 858.1(2) 1205.3(3) 1551.9(3)	86.50(9) 74.85(7) 82.90(8) 87.86(2) 73.55(2) 81.76(2)	$Pt^{II}P_2CHAg$ $Ag^{I}HOPt$	P 228.3(3,0) C 207.3(2) μH 167.4(4) μH 183.1(5) H_2O 225.9(4)	Ag 275.0(3) H 103.3(2)	P,P 175.3(1) H,C 172.9(2) H,Ag 40.4(3) P,Ag 90.2(1,5) C,Ag 146.7 not given	82
$[(NH_3)_2Pt(\mu\text{-}\eta^2\text{-}1\text{-}meu)_2.Cu(H_2O)_2]SO_4.4.5H_2O$ (green)	tr $P\bar{1}$ 2	1039.8(10) 1077.3(8) 1177.2(9)	102.88(6) 102.62(7) 105.05(7)	$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt$	H_3N 201.5(20,15) μηN 200(2,0) μηO 194.5(2,25) H_2O 200(2,4)	Cu 276.5(3)	N,N 90.0(9,2.3) 177.1(9,4) O,O 87.5(8,4.1) 175.0(8,1.7)	83
$(NBu_4)[Cl(C_6Cl_5)_2.Pt(\mu\text{-}Cl)Ag(PPh_3)]$ (pale yellow)	m $P2_1/n$ 4	2007.6(6) 2850.7(5) 947.9(3)	 97.13(3)	$Pt^{II}C_2Cl_2Ag$ $Ag^{I}ClPPt$	C 206.5(9,1) Cl 229.5(2) μCl 233.1(2) μCl 266.7(3) P_{Ph} 239.5(2)	Ag 278.2(1) Cl 67.24(6)	C,C 177.3(3) Cl,μCl 176.7(1) C,Cl 89.2(3,2) C,μCl 90.8(2,2.4) μCl,Ag 62.16(6) μCl,P 118.74(9) μCl,Pt 50.60(5) P,Pt 163.42(8)	84
$[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)\ldots Au(PPh_3)].ClO_4.2EtO$ at 288K	tr $P\bar{1}$ 2	2286.6(7) 1384.4(5) 1139.2(4)	110.79(3) 85.13(2) 96.95(2)	$Pt^{II}P_2HCAu$ $Au^{I}HPPt$	P 232.3(7,11) μH not given C 209.9(12) μH not given P 229.3(8)	Au 279.2(1) H not given	P,P 176.3(2) P,C 90.6(6,9) P,Au 90.1(1,3.6) C,Au 157.3(5) P,Pt 160.9(2)	85
$(NBu_4)[(C_6F_5)_2ClPt(\mu\text{-}Cl).Ag(PPh_3)].0.1CH_2Cl_2$ (pale yellow)	tr $P\bar{1}$ 2	1271.0(3) 1886.5(5) 1213.9(5)	103.10(3) 114.44(2) 77.07(2)	$Pt^{II}C_2Cl_2Ag$ $Ag^{I}ClPPt$	C 207.5(20,25) Cl 229.6(5) μCl 233.9(5) μCl 247.3(6) P 235.0(6)	Ag 279.6(2) Cl 71.0(1)	C,C 175(1) Cl,μCl 178.4(2) C,Cl 89.8(6,1.1) C,μCl 90.4(6,4) μCl,Ag 56.8(1) μCl,P 161.6(2) μCl,Pt 52.3(1) P,Pt 145.2(2)	86
$\{(\eta^2\text{-}mppm)Pt(\mu\text{-}\eta^2\text{-}S_2CNMe_2).Ag(PPh_3)]ClO_4.1.5CHCl_3$ (pale yellow)	tr $P\bar{1}$ 2	1331.2(4) 1414.5(5) 1479.3(5)	112.19(3) 99.97(3) 101.18(3)	$Pt^{II}S_2CPAg$ $Ag^{I}SPPt$	S 240.5(2) μS 236.9(2) C 206.2(7) P 224.0(2) μS 259.4(2) P 238.3(2)	Ag 287.5(1) S 70.6(1)	S,μS 74.1(1)[d] C,P 85.0(2)[e] μS,C 93.4(2) S,P 107.7(1) μS,P 165.0(1) μS,Pt 51.0(1) P,Pt 131.5(1)	87
$[(\eta^1\text{-}PhC{+}C)_2Pt(\mu\text{-}\eta^2\text{-}dppm)_2Au].PF_6.H_2O$ (white)	tr $P\bar{1}$ 2	1114.6(4) 1451.2(2) 2032.2(3)	81.55(1) 101.27(2) 109.35(2)	PtC_2P_2 AuP_2	ηC 195.6(11,2) μηP 230.3(3,4) μηP 231.9(3,4)	Au 291.0(1)	C,C 177.0(4) P,P 175.7(1) C,P 89.2(3,3.3) P,P 174.0(1)	88
$(Ph_3P)(C_6Cl_5)ClPt(\mu\text{-}Cl).Ag(PPh)_3$	m $P2_1/n$ 4	1427.0(2) 1466.3(2) 2002.4(2)	 93.58(1)	$PtCl_2CP$ AgClP	Cl 230.6(3) μCl 234.1(3)] C 203.6(12) P 233.4(3) μCl 251.4(2) P 238.2(3)	Ag 294.5(1) Cl 74.6(1)	Cl,Cl 172.9(1) C,P 172.6(3) μCl,C 86.5(3,3) μCl,P 93.4(1,1.7) Cl,P 162.8(1)	89
$(PEt_3)(H)Pt\{\mu\text{-}\eta^2\text{-}(H)\text{-}7,8\text{-}Me_2C_2B_9H_9\}Au(PPh_3)$	m Cc 4	1192.2(3) 2023.5(7) 1899.8(6)	 96.10(3)	PtH_2P_2 AuBP	H 165 176 P 229.8(5,2) B 222(2) P 227.4(2)	Au 300.0(1)	H,H 169 P,P 163.6(2) H,P 82; 95 B,P 172.0(5)	90

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 member metallocyclic ring. [d]Four member metallocyclic ring. [e]Five member metallocyclic ring.

bond length is somewhat longer at 291.5(1) pm. A red Pt/Mo derivative [113] has a μ-SO_2 group and a μ-η^2-dppa-P,P' ligand acting as bridges between Pt and Mo with a bond length of 293.32(10) pm and Pt-S-Mo bond angle of 75.94(3)°.

In a Pt/Ta derivative [132] two μ-CH_2 groups serve as bridges between the metal atoms. Unfortunately the relevant structural data is not available.

The data in Table 3 cover more than fifty Pt/M derivatives with six different transition metals of which W is the most abundant at 34 examples, with 8 Mo derivatives, 6 Cr, 3 Ti, and 2 each for V and Ta. These come in four crystal classes; monoclinic (32), triclinic (9) orthorhombic (7) and tetragonal (2 examples).

The shortest Pt-M bond is 249.5(2) pm for M = Cr [91]. The bond lengths follow the order: 260.4(7) pm (M = V)

[91] < 264.6 pm (range 249.5(2) [91] - 290.5(2) pm [117], M = Cr) < 278.6 pm (range 260.2(1) [92] - 294 pm [131], (M = W) < 285.3 pm (range 276.6(1) [103] - 293.3(1) pm [113], M = Mo) < 286.0 pm (range 278.9(3) [108] - 296.2(2) pm [102], M = Ti).

There are three examples which contain two crystallographically independent molecules differing mostly by degree of distortion of the M-M, M-L and L-M-L parameters; Pt(μ-η^2-4-mpyt)$_4$CrCl] [91], [(η^4-C$_8$H$_{12}$)Pt(μ-CO){C(C$_6$H$_4$Me-4)CO}W(PMe$_3$)(η^5-cp)] [97] and [Et$_3$P)$_2$Pt(μ-η^5-C$_2$B$_9$H$_9$Me$_2$)W(CO)$_3$](1) [(Et$_3$P)$_2$Py(μ-H) μ-η^5-mtub)W(CO)$_2$(PMe$_3$)](2) [Et$_3$P)Pt(μ-H){μ-η^5-C$_2$B$_9$H$_7$(Et)Me$_2$}W(CO)$_3$](3) [93]. These are examples of distortion isomerism [76]. The latter example [93] also contains chemically in equivalent molecules, with 40% of molecule (1) and 30% each of molecules (2) and (3). The molecules (2) and (3) are disordered.

Table 3. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L – M [°]	L – M - L [°]	Ref.
[Pt(μ-η^2-4-mpyt)$_4$CrCl][c] (orange red)	m P2$_1$/n 8	1645.7(3) 1894.5(3) 1867.1(3)	 101.39(1)	Pt^{II}S$_4$Cr	μηS[b] 229.9(4,5) 232.7(4,2)	Cr 249.5(2)	S,S[b] 90.0(1,5)	91
				Cr^{III}N$_4$ClPt	μηN 209(1,2) Cl 233.4(4)		N,N 90.0(4,1.9) N,Cl 91.5(3,6) Cl,Pt 178.2(1)	
				Pt^{II}S$_4$Cr	μηS 232.0(4,3) 233.1(4,7)	Cr 249.9(2)	S,S 90.0(1,2.1)	
				Cr^{III}N$_4$ClPt	μηN 211(1,2) Cl 234.7(4)		N,N 90.0(4,3.4) N,Cl 91.5(3,1.9) Cl,Pt 179.2(1)	
[Pt(μ-η^2-4-mpyt)$_4$. Cr(OH)].2MeCN (yellow)	tg P4/ncc 4	1492.9(5) 1432.0(7)		Pt^{II}S$_4$Cr	μηS 232.1(3)	Cr 250.9(3)	S,S 90.00(1) S,Cr 90.20(7)	91
				Cr^{III}N$_4$OPt	μηN 210.1(9) HO 189(1)		N,N 89.99(1) N,O 90.7(2) N,Pt 89.3(2)	
[(Et$_3$P)$_2$Pt(μ-CO)$_2$. W(η^2-C$_2$H$_4$)(η^5-cp)]. BF$_4$ (pale orange)	m P2$_1$/c 4	848.1(2) 1424.6(3) 2348.8(7)	 92.76(2)	PtC$_2$P$_2$W	μOC 233(2,2) P$_{Et}$ 230.3(4,4)	W 260.2(1) C 76.0(5,2)	C,C 95.2(5) P,P 98.8(1) C,P 116.0(4,2.1) C,W 47.7(4,7) P,W 130.6(1,1.5)	92
				WC$_9$Pt	μOC 199(2,3) η^{2}C 227(2,1) η^{5}C not given		μC,μC 112.1(6) C,C 36.7(6)[d] μC,Pt 56.3(5,9) C,Pt 105.5(5,2)	
[(Et$_3$P)$_2$Pt(μ-CO)$_2$. W(η^6-mtub)].CH$_2$Cl$_2$ (orange)	m P2$_1$/c 4	1189.3(2) 1523.3(3) 2215.3(3)	 93.35(1)	PtC$_2$P$_2$W	μOC 217(2,1) P$_{Et}$ 230.5(5,4)	W 260.2(1) C not given	P,P 106.9(2) P,W 126.5(1,1.3)	93
				WC$_4$B$_2$Pt	μOC 207(2,1) η^{6}C 203(2,1) η^{6}B 233(2,0) 246(2,6)		μC,μC 107.8(6)	
[Pt(μ-η^2-4-mpyt)$_4$VO]. tol (red)	tg P4/ncc 4	1535.0(2) 1427.0(3)		Pt^{II}S$_4$V	μηS 232.3(1)	V 260.4(7)	S,S 89.99(1) S,V 90.8(2)	91
				V^{IV}N$_4$OPt	μηN 213(2) O 159(3)		N,N 89.80(7) N,O 93.4(6) N,Pt 86.6(6)	
[(Me$_3$P)$_2$Pt{μ-C(CO$_2$Me). Ph}(μ-CO)Cr(CO)$_3$(PMe$_3$)] (orange)	m A2/a 8	1827(3) 984(1) 31.93(1)	 106.2(1)	PtC$_2$P$_2$Cr	μC 198(3) μOC 219(4) P$_{Me}$ 225(1) 232(1)	Cr 264.6(7) C 80(2,4)	C,C 87(2) P,P 98.3(5) C,P 89(1,2) 162(1,6) C,Cr 41(1); 56(1) P,Cr 112.9 143.7(4)	94
				CrC$_5$PPt	OC 188(5,5) μOC 175(5) μC 227(4) P$_{Me}$ 235(2)		μC,μC 90(2) μC,P 102; 162(1) μC,Pt 55(1) P,Pt 141.9(4)	
[(Et$_3$P)(Ph)Pt(μ-H)$_2$. W(η^5-cp)$_2$].BPh$_4$	tr P$\bar{1}$ 2	1575.9(3) 1404.5(3) 946.7(2)	89.9(2) 107.0(2) 88.8(2)	Pt^{II}H$_2$CPW	μH not given C$_{Ph}$ 201(1) P$_{Et}$ 221.5(5)	W 266.3(1) H not given	C,P 88.2(5) C,W 134.0(2) P,W 137.8(1)	95
				W^{IV}C$_{10}$H$_2$Pt	ηcp 229(3,4) μH not given		cp,cp 141.0(8)	
[(PhMe$_2$P)$_2$Pt. (μ-CC$_6$H$_4$Me-4). (μ-σ-η^5-C$_2$B$_9$H$_8$Me$_2$). W(CO)$_2$].4CH$_2$Cl$_2$ (purple)	m P2$_1$/c 4	1339.9(5) 2519.6(6) 1231.9(2)	 110.73(2)	PtP$_2$CBW	P 227.1(4) 236.6(4) μC 214(1) μB 217(1)	W 272.0(1) C not given	P,P 95.0(1) C,P 89.0(4) 162.1(3) B,P 89.8(4) 154.1(4) C,W 43.9(3)	96
				WC$_5$B$_3$Pt	OC 199(2,1) μC 189(1) μηC 250(1,2) B 236(2,1) μB 221(5)		C,C 90(1) μC,Pt 51.6(4)	

Continued **Table 3.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$(\eta^4\text{-}C_8H_{12})Pt(\mu\text{-}CO).\{\mu\text{-}C(C_6H_4Me\text{-}4)CO\}.W(PMe_3)(\eta^5\text{-}cp)$[c]	m $P2_1/c$ 8	2249.2(7) 1224.1(6) 2043.0(7)	 106.07(3)	PtC_6W	ηC 222(3,3) μC 206.4(15) μOC 229(2)	W 272.0(1) C 80.2(6)	μC,W 48.4(5,3.2)	97
				WC_8PPt	C 214(2) μC 216(2) μOC 196(2) ηcp not given P_{Me} 240.5(6)		μC,μC 103.8(7) μC,C 37.6(6)[d] μC,Pt 52.2(4,3.8)	
				PtC_6W	ηC 224(2,4) μC 206(2) μOC 227.3(15)	W 272.8(1) C 80.3(6)	μC,W 47.8(5,2.8)	
				WC_8PPt	C 211(2) μC 217(2) μOC 192(2) P_{Me} 240.2(4)		μC,μC 102.9(7) μC,C 39.4(5)[d] μC,Pt 51.7(5,3.1)	
$(Et_3P)Pt(\mu\text{-}CC_6H_3Me_2\text{-}2,6).(\mu\text{-}\eta^5\text{-}C_2B_9H_8Me_2)W(CO)_2$ (red)	m $P2_1/c$ 4	1584.5(11) 1345.4(6) 1572.5(12)	 117.98(5)	PtCPW	μC 215(2) μB 201(2) P_{Et} 225.1(7)	W 272.8(1) C 85.0(6)	μC,P 160.6(4) μB,P 100.6(6)] μC,W 43.2(4) μB,W 55.4(6) P,W 155.9(1)	98
				WC_5B_3Pt	OC 196(2,3) μC 188(2) μηC 251(2,0) μηB 235(3,6)		C,C 90.0(8) μC,Pt 51.8(5)	
$(Et_3P)(OC)Pt.(\mu\text{-}CC_6H_3Me_2\text{-}2,6).(\mu\text{-}\eta^5\text{-}C_2B_9H_8Me_2).W(CO)_2$ (red)	tr_ P1 2	1041.6(10) 813.3(3) 1850.8(15)	89.91(5) 95.46(7) 103.52(6)	PtC_2BPW	OC 193(1) μC 229(1) μB 216(1) P_{Et} 229.4(3)	W 272.8(1) C 80,8(4)	μC,P 178.3(3) μB,P 87.0(3) μC,W 43.2(3) μB,W 54.2(3) P,W 138.5(1)	98
				WC_5B_3Pt	OC 202(2,3) μC 189(1) μηC 247(1,1) μηB 233(1,5)		C,C 91.9(6) μC,Pt 55.9(3)	
$[(PhMe_2P]_2.Pt(\mu\text{-}CC_6H_4Me\text{-}4).\{\mu\text{-}\eta^6\text{-}C_2B_{10}H_9Me_2).W(CO)_2]$ (orange)	m $P2_1/n$ 4	1393.0(5) 1857(1) 1633.1(6)	 105.45(3)	PtP_2CBW	P_{Et} 228.4(3) 236.2(3) μC 214(1) μB 215(1)	W 273.8(1) C not given	P,P 94.8(1) P,μC 88.1(3) 168.2(2) P,μB 87.2(3) 161.5(3) μC,W 44.3(3)	96
				WC_5B_4Pt	OC 202(2,1) μC 192(1) μηC 235(1,4) μηB 246(2,9) μB 223(1)		C,C 90.1(1) μC,Pt 51.0(3)	
$(PhMe_2P)_2(\mu\text{-}CC_6H_4Me\text{-}4).W(CO)_2(\eta^5\text{-}cp)$ (red)	m $P2_1/c$ 4	1221.2(11) 933.9(6) 2612.5(24)	 92.77(7)	PtP_2CW	P 225.8(2) 232.5(2) μC 199.7(9)	W 275.1(1) C 87.9(3)	P,P 99.4(1) P,μC 99.7(2) 160.6(3) P,W 115.3(1) 145.2(1) μC,W 45.6(2)	99
				WC_8Pt	OC 196.7(8,3) μC 196.7(6) ηcp 236(1,2)		C,C 90.4(3) C,μC 101.7(3,1.7) μC,Pt 67.4(2)	
$[(Et_3P)_2\{\eta^1\text{-}C(CHC_6H_5)H\}.W(CO)_3(\eta^3\text{-}dppe)].BF_4.CHCl_3$ (orange)	tr_ P1 2	1568.9(3) 1619.2(4) 1179.9(2)	93.69(2) 95.66(2) 89.98(2)	PtP_2CW	P_{Et} 226.5(10,7) C 196(4)	W 275.1(2) C 74.2(12)	P,P 101.7(4) P,C 84.4(12) 171.4(12) P,W 112.1(3) 145.9(3) C,W 62.6(12)	100
				WC_3P_2Pt	OC 188(4) 211(4,2) ηP 241.8(10) 266.8(10)		P,P 81.1(3) P,Pt 121.4(2) 142.9(2)	
$(PhMe_2P)_2Pt(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)W(CO)_2(\eta^5\text{-}cp)$ (purple)	m $P2_1/c$ 4	1221.1(11) 933.9(6) 2612.5(23)	 92.77(7)	PtP_2CW	P not given μC 205(2)	W 2753(1) C not given	μC,W 70	101
				WC_8Pt	OC not given ηC_{cp} not given μC 196(2)		not given	

Continued **Table 3.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$(Ph_3P)Pt(\mu\text{-}PPh_2)_2W(CO)_4$ (yellow)	m $P2_1/c$ 4	1167.2(2) 1872.6(3) 1986.9(3)	 96.08(1)	PtP_3W WC_4P_2Pt	P_{Ph} 223.4(3) μP 225.8(3,9) OC 200.2(14,19) μP 250.8(4,1)	W 276.4(1) P 70.8(1,2)	P,μP 121.1(1,9) μP,μP 117.8(1) P,W 177.4(1) μP,W 58.9(1,1) C,C 89.6(5,1.2) 178.2(5) μP,μP 100.8(1) C,μP 88.6(4,4.6) 176.8(4,3.0) C,Pt 90.9(4,5) 135.0(4,9) μP,Pt 50.4(1,2)	102
$(Et_3P)Pt(\mu\text{-}PPh_2)_2Mo(CO)_4$ (orange)	or Pbca 8	1838.1(3) 1698.9(2) 2246.2(5)		PtP_3Mo MoC_4P_2Pt	P_{Et} 223.4(3) μP 225.4(2,1) OC 201.9(11,20) μP 250.6(3,6)	Mo 276.6(1) P 70.85(7,13)	P,μP 121.2(1,1.0) μP,μP 117.67(9) P,Mo 178.82(9) μP,Mo 58.85(7,16) C,C 91.3(4,3.7) 177.6(4) μP,μP 100.60(8) C,μP 87.2(3,6.3) 176.7(3,1.8) C,Pt 89.6(3,2.1) 132.5(3,1.3) μP,Pt 50.31(6,3)	103
$[(Me_3P)_2Pt(\mu\text{-}CO)$. $\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}$. $W\{\eta^2\text{-}C(Me){=}CMe\}$. $(\eta^5\text{-}cp)].BF_4$ (red)	m $P2_1/n$ 4	1064.7(6) 1021.4(7) 3249.4(16)	 99.21(4)	PtC_2P_2W WC_9Pt	μOC 217.3(19) μC 211.0(15) P_{Me} 231.3(6,4) μOC 199.7(17) μC 210.1(18) ηC 203.3(22,11) ηcpC 236.5(16,32)	W 277.1(1) C 82.8(7,5)	μC,μC 93.6(7) P,P 99.5(2) μC,P 87.7(5,1.4) 157.3(5,4.2) μC,W 47.2(4,1.5) P,W 130.2(1,4.7) C,C 36.5(8)[d] μC,μC 99.2(7) μC,Pt 50.1(5,1.1)	104
$(\eta^2\text{-}dppm)Pt$. $(\mu\text{-}C{=}CH_2)W(CO)_5$ (yellow)	m $P2_1/c$ 4	932.5(2) 1783.7(3) 1945.1(3)	 105.74(1)	PtP_2CW WC_6Pt	ηP 225.0(3) 233.5(2) μC 201.2(9) OC 202.9(12,20) μC 219.8(8)	W 277.4(1) C 82.3(3)	P,P 73.3(1)[e] P,μC 106.8(2) 174.8(3) P,W 127.8(1) 158.4(1) μC,W 51.7(2) C,C 89.6(4,6.5) 173.5(4,8) C,μC 77.4 -109.7(4) μC,Pt 46.0(2)	105
$(PhMe_2P)(Me)$. $Pt(\mu\text{-}CH_2)(\mu\text{-}Me)$. $Ti(\eta^5\text{-}cp)_2$ (orange red)	m $P2_1/n$ 4	1333.3(4) 1168.6(2) 1435.1(3)	 115.03(2)	PtC_3PTi TiC_{12}	C_{Me} 210.8(6) μH_2C 207.8(1) μC_{Me} 212.2(8) P 227.9(2) C_{cp} not given μH_2C 211.5(7) μC_{Me} 239.5(8)	Ti 277.6(1) C 75.6(2) 82.9(3)	μC,μC 105.7(3) μC,P 87.6(2) C,P 86.3(2) μC,μC 95.7(2)	106
$(NEt_4)[Cl_2Pt(\mu\text{-}S)_2$. $W(\eta^3\text{-}HBpz_3)(S)]$ (purple)	or Pbca 8	1727.1(4) 1896.1(2) 2033.7(5)		$PtCl_2S_2W$ WN_3S_3Pt	Cl 233.6(3,6) μS 228.9(3,2) ηN 225.3(9,10) S 214.8(3) μS 226.1(3,2)	W 277.92(6) S 75.31(9,1)	Cl,Cl 87.3(1) S,S 100.9(1) Cl,S 86.8(1,9) 167.4(1,2.5) N,N 79.1(3,1.8)[f] μS,μS 102.7(1) S,μS 102.6(1,9)	107
$[(Ph_3P)Pt(\mu C{+}CBu^t)_2$. $Ti(\eta^5\text{-}cp)].0.5thf$ (dark red)	m C2/c 8	2167.4(4) 934.3(2) 3642.5(7)	 92.23(3)	PtC_3PTi TiC_{12}	C 219.1(15) μC 199.0(13) 205.4(13) P_{Ph} 224.7(3) C_{cp} not given μC 210.2(14) 243.5(14)	Ti 278.9(3) C 77.4(5) 84.3(5)	μC,μC 107.0(6) μC,C 140.6(5) μC,P 108.6(4) C,P 110.7(4) μC,μC 91.3(5)	108

Continued **Table 3.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
(η^2-MeO$_2$C+CCO$_2$Me). Pt(μ-PPh$_2$)$_2$W(CO)$_4$ (yellow)	m P2$_1$/n 4	1143.8(4) 1109.5(4) 1776.4(6)	 95.55(2)	PtC$_2$P$_2$W WC$_4$P$_2$Pt	ηC 203.5(9,1) μP 228.4(3,2) OC 203.1(11,17) μP 243.9(3,4)	W 279.5(1) P 72.5(1,1)	C,C 37.5(4)[d] μP,μP 112.5(1) C,μP 105.1(3,5) 142.3(3,5) C,W 161.1(3,1) μP,W 56.3(1,1) C,C 90.1(4,5.1) 175.4(4) μP,μP 102.2(1) μP,Pt 51.2(1,1)	102
[(Me$_3$P)$_2$Pt(μ-CO). (μ-CHC$_6$H$_4$Me-4). W(CO)(η^5-cp)].BF$_4$ (yellow)	m P2$_1$/c 4	1390.3(3) 1621.3(3) 1185.9(2)	 96.89(2)	PtC$_2$P$_2$W WC$_8$Pt	μOC 227.2(16) μC 205.3(14) P$_{Me}$ 228.1(4) 231.4(4) OC 196.6(17) μOC 195.6(15) μC 216.6(14) ηC$_{cp}$ 232.3(14,53)	W 279.5(1) C 82.7(5,3)	P,P 97.9(1) μC,P 88.2(4,1.6) 168.3(5,3.8) μC,W 47.1(4,3.2) P,W 130.2(1,8.4) μC,Pt 50.3(4,3.5)	109
[(Et$_3$P)$_2$(μ-CO). (μ-CC$_6$H$_4$Me-4)Pt. W(CO)(η^5-cp)].BF$_4$ (yellow)	or Pca2$_1$ 4	1824.0(4) 1123.1(3) 1581.7(4)		PtC$_2$P$_2$W WC$_8$Pt	μOC 223(3) μC 201(3) P$_{Et}$ 230.9(5,4) OC 195(3) μOC 199(3) μC 222(2) ηC$_{cp}$ 229(3,6)	W 279.7(1) C not given	P,P 98.4(2) μC,W 48.4(6,3.6) P,W 119.8(2) 141.7(2) μC,Pt 48.9(6,3.5)	110
(η^2-dppe)Pt(μ-CO). (μ-H$_2$C=CCO$_2$Me). Mo(CO)(η^5-cp)	m P2$_1$/n 4	1189.3(4) 1535.0(5) 1920.8(6)	 102.47(3)	PtC$_2$P$_2$Mo MoC$_9$Pt	μOC not given μC 195(4) ηP 225(1,3) OC not given μOC not given μC 220(5) C 227(4) ηC$_{cp}$ not given	Mo 280.6(2) C not given	not given not given	111
(Ph$_3$P)(OC)Pt. (μ-PPh$_2$)W(CO)$_2$. (η^5-cp^c) (yellow)	tr P$\bar{1}$ 4	1157.3(3) 1426.4(3) 2168.1(4)	85.96(2) 82.80(2) 70.65(2)	PtP$_2$CW WC$_7$PPt	P$_{Ph}$ 231.2(3) μP 228.7(3) OC 184.8(13) OC 190.1(13,5) ηC$_{cp}$ not given μP 237.7(3)	W 281.0(1) P 74.0	P,μP 105.4 P,C 107 μP,W 54.5 C,W 93.1 C,Pt 78.1 125.0 μP,Pt 51.5	112
(Ph$_3$P)Pt(μ-inst). (μ-η^2-dppa)W(CO)$_4$ (orange)	or Pbca 8	2055.0(13 2209.8(14) 2605(5)		PtP$_2$CW WC$_5$P	P$_{Ph}$ 227.1(3) μηP 230.3(3) OC 194.4(11) OC 200(2,3) μC$_{cp}$ 230.9(10) μηP 249.8(3)	W 281.0(2) C 82.2(4)	P,P 108.6(1) P,μC 97.9(3) 151.0(3) μC,W 54.5(3) μC,Pt 43.3(3) P,Pt 75.94(7)	113
[(Ph$_3$P)(OC)Pt. (μ-η^6-C$_2$B$_{10}$H$_{10}$Me$_2$). Mo(CO)$_3$].0.5CH$_2$Cl$_2$ (red)	tr P$\bar{1}$ 2	920.23(5) 1380.17(6) 1513.52(8)	109.376(4) 91.059(4) 101.054(4)	PtHCBPMo MoC$_5$B$_4$Pt	H 150 μB 231.3(8) OC 185.1(6) P$_{Ph}$ 230.5(2) OC 199.5(8,19) μηC 227.7(6) 250.2(8) B 242.3(8,50) μB 236.2(7)	Mo 281.4(1) B not given	H,C 168.8(4) μB,P 114.2(2) H,P 92.8(3) C,μB 146.3(3) C,P 98.4(2) H,Mo 75.3(3) C,Mo 93.5(2) P,Mo 168.0(1) C,Pt 77.2(2,3.9) 144.0(2)	114
(OC)Pt{μ-C(OMe). C$_6$H$_4$Me-4}(μ-η^2-dppm). W(CO)$_4$ (orange)	m P2$_1$/n 4	1299.8(15) 2783.2(19) 1217.6(7)	 111.74(6)	PtC$_2$PW WC$_5$PPt	OC 183(4) μC 197(3) μηP 233.5(6) OC 203(3,6) μC 249(3) μηP 254.4(7)	W 281.8(3) C 77.3(9)	C,μC 104.4(12) C,P 97.4(9) μC,P 157.9(8) C,W 163.8(9) μC,W 59.6(8) P,W 98.7(2) μC,P 116.9(5) μC,Pt 43.1(5)	115

Continued **Table 3.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$[(Et_3P)_2Pt\{\mu-\eta^5-C_2B_9H_9Me_2)W(CO)_3]$[91] **$[(Et_3P)_2Pt(\mu-H)(\mu-\eta^5-mtub)W(CO)_2(PMe_3)]$[92]** **$[(Et_3P)_2Pt(\mu-H)\{\mu-\eta^5-C_2B_9H_7(Et)Me_2\}W(CO)_3]$[93]** **(orange)**	m $P2_1/n$ 8	1739.0(3) 1773.1(6) 2122.0(4)	 100.68(1)	PtP_2HBW	P_{Et} 226.9(4) 231.1(3) H 106(13) μB 241(2)	W 281.8(1) B not given	P,P 97.0(1) H,B 21(7) P,H 156(6) P,W 106.6(1) 156.4(1) B,W 51.9(4)	93
				WC_5B_3Pt	OC 195(2,1) μηB 233(2,2) μB 232(2) C 238(2,0)		C,C 78.9(6,6) 103.1(6) C,Pt 76.4(4,3) 139.8(5)	
				PtP_2HBW	P_{Et} 226.0(4) 237.0(4) μH 220(10) μB 215(2)	W 290.2(1) H 105(7) B 81.1(6)	P,P 101.9(1) H,B 74(3) P,H 92(3); 164(3) P,B 91.9(4) 165.6(4) P,W 115.3(1) 142.2(1) H,W 28(3) B,W 51.8(4)	
				WC_5B_3HPt	OC 194(2,4) μηC 239(1,1) μηB 239(2,1) μημB 231(1)		C,C 76.3(7,4) 102.1(7) H,Pt 47(5)	
$(Me_3P)_2Pt\{\mu-C(CH_2).C_6H_4Me-4\}W(CO)_2(\eta^5-cp)$ **(orange)**	m $P2_1/n$ 4	1318.1(3) 1260.8(3) 1493.6(4)	 96.95(2)	PtP_2CW	P_{Me} 225.7(4) 230.1(4) μC 202(1)	W 282.0(1) C 83.8(4)	P,P 98.8(3) P,μC 92.9(4) 165.8(4) P,W 118.4(1) 142.7(1) μC,W 50.8(3)	116
				WC_9Pt	OC 194(2,2) μC 220(1) C 232(1) μC_{cp} 235(2)		C,Pt 65.9(4,4.7) μC,Pt 45.4(3)	
$(\eta^3$-coc)Pt(μ-CO). **(μ-PPh_2)$Cr(CO)_4$** **(brown)**	m Cc 4	2521.2(3) 1017.2(2) 957.7(2)	 90.53(1)	PtC_4PCr	ηC 207.3(7) 227.3(7,2) μOC 225.2(7) μP 223.9(2)	Cr 282.0(1) P 75.93(6) C not given	μC,C 164.9(3) μC,P 97.2(2)	117
				CrC_5PPt	OC not given μOC 197.6(7) μP 234.2(2)		μC,P 102.2(2)	
$(Me_3P)_2Pt.$ **$\{\mu-C(OMe)C_6H_4Me-4\}.$** **$W(CO)_4(PMe_3)$** **(brown orange)**	or $Pna2_1$ 4	1818.0(6) 1072.0(3) 1469.7(4)		PtP_2CW	P_{Me} 223.6(4) 232.6(3) μC 203(1)	W 282.5(1) C 79.4(4)	P,P 99.9(1) P,μC 94.6(3) 165.3(3) P,W 110.0(1) 150.1(1) μC,W 55.7(3)	118
				WC_5PPt	OC 199(2,4) μC 237(1) P_{Me} 250.7(4)		μC,P 92.4(3) μC,Pt 45.0(3) P,Pt 127.7(1)	
$[(\eta^1-C_6F_5)_2.$ **$Pt(\mu-C{=}CBu^t)_2.$** **$Ti(\eta^5-cp)_2].CH_2Cl_2$** **(red)**	m $P2_1/n$ 4	1372.5(2) 1587.5(2) 1642.493)	 99.58(2)	PtC_4Ti	ηC 205.1(9,8) μC 201.7(11,3)	Ti 283.1(2) C 83.2(4)	μC,μC 103.8(4) C,C 85.7(4)	119
				$TiC_{12}Pt$	ηC_{cp} not given μC 224.8(10,8)		μC,μC 89.8(4)	
$(\eta^4$-cod(Ph)PtMo$(CO)_3.$ **$(\eta^5$-cp)** **(deep red)**	m $P2_1/n$ 4	1429.1(5) 1273.8(3) 1198.8(4)	 112.01(3)	PtC_5Mo	ηC 220.8(15,12) 235.6(15,16) C_{Ph} 205.4(14)	Mo 283.20(12)	C,C 90.6(6) 162.9(5,1.1) C,Mo 84.0(4) 100.1(4,2.2) 162.0(4,3.8)	120
				MoC_8Pt	OC 195.6(16,52) ηC_{cp} 233.6(29,49)		C,C 88.4(7,6) 113.4(6) C,Pt 58.1(4,6) 102.5(5)	
$(Et_3P)_2Pt(\mu-H).$ **$(\mu-\eta^5$-dub)W.** **$(CO)_2(PMe_3)$** **(orange)**	tr $P\bar{1}$ 2	1137.6(7) 1638.0(7) 1100.0(6)	100.44(4) 85.92(5) 93.15(4)	PtP_2HBW	P_{Et} 225.4(3) 237.0(2) μH 188(6) μB 212.3(5)	W 284.3(2) H 113(3) B 80.6(2)	P,P 103.8(1) H,B 74(2) P,H 88; 161(2) P,B 93.9; 162.1(2) H,W 30(2) B,W 51.9(2)	93
				WC_4B_3HPPt	OC 197.7(6,1) ηC 238.5(5,40) ηB 226.9(6) 241.3(6,8) μH 153(5) P_{Me} 248.1(2)		H,P 130(2) H,Pt 37(2) H,Pt 144.4(1)	

Continued Table 3. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
(η⁴-cod)(Ph)PtW(CO)$_3$. (η⁵-cp) (deep red)	m $P2_1/n$ 4	1429.1(3) 1273.1(2) 1202.7(3)	112.48(2)	PtC_5W WC_8Pt	ηC 220.5(14,19) 237.3(14,8) C_{Ph} 201.4(13) OC 196.4(14,24) $ηC_{cp}$ 230.9(24,55)	W 284.35(7)	C,C 78.6 - 94.2(5) 162.3(5,1.9) C,W 43.0(3,2) 84.8(4) 100.4(4,1.6) 164.9(4) C,W 58.6(4,4) 103.6(4)	121
[ClPt(μ-CO)(μ-η²- $Ph_2Ppy)_2$. $Mo(CO)_2Cl].CH_2Cl_2$ (red)	or I2cb 8	1378.4(6) 1767.7(5) 31.91.5(13)		PtP_2CClMo MoN_2C_3ClPt	μηP 222.7(5) 234.8(5) μOC 221.8(17) Cl 232.4(4) μηN 230.8(17,7) OC 192.9(20,22) μOC 195.4(14) Cl 252.1(4)	Mo 284.5(1) C not given	P,P 166.1(2) C,Cl 144.0(5) P,C 89.5(5,2.0) P,Cl 94.5(2,1.1) P,Mo 84.9(1,4) C,Mo 43.2(4) Cl,Mo 172.5(1) C,Pt 109.6(5,1.7) μC,Pt 51.0(5) Cl,Pt 161.7(1)	122
$(Me_3P)_2$Pt{μ-C(OMe)Ph}. $W(CO)_5$ (orange)	tr $P\bar{1}$ 2	972.8(5) 1600.2(13) 961.1(6)	109.86(6) 116.34(4) 83.77(6)	PtP_2CW WC_6Pt	P_{Me} 225.3(3) 233.5(3) μC 204(1) OC 204(1,5) μC 248(1)	W 286.1(1) C 77.8(3)	P,P 99.3(1) P,C 95.4(4) 164.8(4) P,W 107.6(1) 152.8(1) C,W 58.0(3) C,C 90.0(6,6.0) 169.7(5,4) C,μC 80.3(5,6.0) 99.5(5,6) μC,Pt 44.2(3)	123
(η²-dppm)Pt(μ-S)$_2$W(S)$_2$ (yellow)	m C2/c 4	1595.2 1030.4 1715.9	108.31	PtS_2P_2W WS_4Pt	μS 234.8(3,0) ηP 225.7(2,0) S 214.5(3,0) μS 223.9(3,0)	W 286.22(7) S 77.2(1)	P,P 73.7(1)[e] S,S 99.4(1) P,S 93.50(9) 166.87(9) S,S 110.7(1) μS,μS 106.2(1) S,μS 110.0(1,1.2)	124
[$(Et_3P)_2$Pt(μ-CO). {μ-η¹:η²-C(H)(NEt$_2$)}. W(CO)(η³-HBpz$_3$)].BF$_4$ (crimson)	m $P2_1$ 2	1089.1(5) 1395.6(4) 1368.4(4)	95.05(3)	PtC_2P_2W WN_4C_3Pt	μOC 228(2) μC 204(3) P_{Et} 229(2) 235.9(14) η³N 225(3,4) μη²N 222(2) μC 219(3) OC 208(4) μOC 208(4)	W 287.1(10) C not given	P,P 98.8(3) μC,W 47.6(7,1.8) P,W 118.4(2) 142.7(2) μC,Pt 48.6(7,3.4) C,Pt 79.4(8)	125
$(Et_3P)_2$Pt(μ-H). (μ-CHC$_6$H$_4$Me-4). W(CO)$_2$(η⁵-cp) (yellow)	m $P2_1/c$ 4	1055.4(4) 1162.4(3) 1939.3(7)	97.64(3)	PtP_2HCW WC_8HPt	P_{Et} 226.5(3) 230.5(3) μH 180 μC 210.9(9) OC 195.2(11,3) μC 225.9(9) $ηC_{cp}$ 234.8(7,63) μH 172	W 289.5(1) H 111 C 83.0(3)	P,P 102.3(1) P,C 92.3(3) 165.1(3) P,W 114.4(1) 142.6(1) C,W 50.7(2) C,C 75.3(4) C,μC 77.8(4) 116.3(4) μC,Pt 46.3(2)	126
[(η²-dppm)Pt. (μ-η²-dppm)W. (CO)$_2$(η⁵-cp)].PF$_6$ (red)	tr $P\bar{1}$ 1	1125.7(7) 1269.1(6) 1105.5(6)	112.20(3) 101.68(3) 76.71(4)	PtP_3W WC_7PPt	ηP 231.7(4,8) μηP 228.8(4) OC 193(1,2) $ηC_{cp}$ not given μηP 238.2(3)	W 290.2(2)	P,P 71.1(2)[e] 101.4(2) 170.8(2) P,W 93.3(1,4.8) 166.3(1) C,C 79.6(6) C,P 77.9(4) 118.3(5) C,Pt 61.6(5) 113.2(5) P,Pt 76.5(1)	127

Continued Table 3. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Ti, V, Ta, Cr, Mo or W)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$(Et_3P)_2Pt(\mu\text{-}PPh_2)Cr(CO)_4$ (green)	m Cc 4	1671.9(9) 1146.8(3) 1827.5(6)	 113.68(3)	PtP_3Cr CrC_4PPt	P_{Et} 228.7(2) 232.2(2) μP 232.1(2) OC 284.4(12,33) μP 232.0(3)	Cr 290.5(2) P not given	P,P 101.5 P,μP 102.0 P,Cr 153.2 μP,Cr 51.2 C,Pt 98.7(-,10.6) 157.0 μP,Pt 51.2	117 128
$[(\eta^2\text{-dppm})Pt.(\mu\text{-}\eta^2\text{-dppm})Mo(CO)_2.(\eta^5\text{-}C_5H_4Me)]_2[Mo_2O_7].CH_2Cl_2$ (red)	m $P2_1/n$ 4	3484.1(6) 2468.6(6) 1292.1(3)	 98.41(1)	PtP_3Mo MoC_7PPt	ηP 233.4(8) 237.3(8) μηP 228.4(6) OC 193(2,1) ηC_{cp} not given μηP 241.7(5)	Mo 291.2(4)	P,P 70.3(2)[e] P,μP 98.8(2) P,Mo 167.9(2) μP,Mo 91.8(2) P,Pt 78.0(2)	129
$(Ph_3P)Pt(\mu\text{-}\eta^2PF_2N(Me).PF_2)_2Mo(CO)_3$ (yellow orange)	or Pbca 8	1454.4(1) 2302.3(1) 1945.3(2)		PtP_3Mo MoC_3P_2Pt	P_{Ph} 231.6(4) ηP 221.1(4,5) OC 201(2,2) ηP 233.1(6,3)	Mo 291.5(1)	P,P 100.3(2,3.1) 158.6(2) P,Mo 81.6(1,4.6) 157.1(1) C,C 88.6(8,1) 177.0(7) P,P 175.9(2) C,P 90.7(7,2.4)	130
$[(Ph_3P)Pt(\mu\text{-}SO)_2(\mu\text{-}\eta^2\text{-dppa})Mo(CO)_4]OPPh_3$	tr $P\bar{1}$ 2	1254.4(3) 1457.5(3) 1920.0(4)	99.78(3) 98.99(3) 103.00(3)	PtP_2SMo MoC_4SPPt	P_{Ph} 229.04(13) μηP 231.67(14) μS 220.00(12) OC 202.8(9,21) μS 253.08(17) μηP 250.2(14)	Mo 293.32(10) S 75.94(3)	P,P 104.47(5) P,μS 152.98(4) P,Mo 97.40(4) 158.13(3) μS,Mo 56.82(4) C,μS 81.4(1,3.2) 102.13; 159.44(17) C,P 87.4(1,1.4) 170.44(15) μS,P 111.24(5) μS,Pt 47.24(3) P,Pt 75.27(4)	113
$(Et_3P)_2Pt(\mu\text{-}S)_2WS_2$ (bright yellow)	m $P2_1/n$ 4	908.1(1) 1451.6(4) 1681.9(3)	 82.33(1)	PtS_2P_2W WS_4Pt	μS 237.5(3,13) P_{Et} 230.2(2,10) S 214.2(3,5) μS 222.5(3,0)	W 294 S 79.57(8,40)	μS,μS 96.09(9) P,P 96.49(8) μS,P 83.71(9,2.42) 177.56(9,18) S,S 109.2(1) μS,μS 104.76(9) S,μS 110.7(1,7)	131
$(PhMe_2P)(Me)Pt(\mu\text{-}CH_2).(\mu\text{-}Me)Ti(\eta^5\text{-cp})_2$ (orange red)	m $P2_1/n$ 4	1324.9(3) 1164.6(3) 1454.2(3)	 114.45(2)	PtC_3PTi $TiC_{12}Pt$	C_{Me} 207.1(15) μH_2C 211.3(17) μC_{Me} 239.9(4) P 226.1(4) ηC_{cp} not given μH_2C 206.6(18) μC_{Me} 242.7(5)	Ti 296.2(2) C 75.7(1) 90.3(7)	C,μC 83.1(6) μC,μC 96.6(5) C,P 87.7(5) μC,P 170.4(5) μC,μC 97.0(5)	106
$(Me_3P)_2Pt(\mu\text{-}CH_2).Ta(Me)(\eta^2\text{-cp})_2$				PtP_2Ta $TaC_{12}Pt$				132
$(Me_3P)(H)Pt(\mu\text{-}CH_2)_2.Ta(\eta^5\text{-cp})_2$				PtC_2HPTa $TaC_{12}Pt$				132

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]Two crystallographically independent molecules. [d]Three member metallocyclic ring. [e]Five member metallocyclic ring. [f]Six member metallocyclic ring. [g]Two crystallographically independent and unequivalent molecules: g_1 = 40%; g_2 and g_3 are disordered (at 30%).

2.2.3 Mn and Re

The data for red, orange and yellow derivatives with Mn or Re are gathered in Table 4. Fifteen are Pt/Re compounds and eight are Re/Mn, and their structures are complex. In several examples the Pt-M bond is spanned by one atom or ligand. Thus a μ-Cl atom bridges a Pt-Mn bond [94,134,137] or a Pt-Re bond [138,140], while a Pt-Mn bond (260.3(1) pm) is spanned by a μ-I atom [133]. In the former examples the Pt-Mn bond length ranges from 262.8(1) to 269.3(1) pm with a mean Pt-Cl-Mn bridge angle of 83°. The Pt-Re bond distances range from 270.69(13) to 273.0(1) pm with mean Pt-Cl-Re bridge angle of 83.3°.

In a yellow derivative [136] the Pt-Re bond of 264.3(1) pm is spanned by a single μ-H atom. In three Pt/Re derivatives [141,142] the Pt-Re bonds are each spanned by a μ-BL ligand with a mean Pt-B-Re bridge angle of 74.5°. Two yellow-gold species [147] have a Pt-Re bond (286.75(5) and 288.15(8) pm) spanned by a μ-Pcy_2 ligand with bridge angles of 77.16(7)° and 76.8(2)°, respectively.

There are two Pt/Mn derivatives [134,135] in which the Pt-Mn bond (262.6(1) and 264.1(1) pm) is doubly spanned by μ-CO and μ-tpm-C, or M-CO and μ-CS, respectively, with mean Pt-C-Mn bridge angles of 80.2° and 83.4°. The Pt-Mn bond (272.8(6) pm) is spanned

Table 4. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Mn or Re)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L – M [°]	L – M - L [°]	Ref.
(MeBu$^t_2$P)η^1-ocp). Pt(μ-I)Mn(CO)$_4$ (orange)	or Pbca 8	1463.4(5) 1954.6(18) 1632.5(5)		PtCPIMn	ηC[b] 188.9(8) P 231.0(2) μI 266.2(1)	Mn 260.3(1) I 58.2(1)	C,P 98.2(3) C,I 155.4(3) C,Mn 94.0(3) P,Mn 167.8(1) P,I 106.4(1) I,Mn 61.4(1)	133
				MnC$_4$IPt	OC 182(1,4) μI 268.9(2)		C,C 94.6(4,6.7) 159.9(4) C,I 88.5(3,3) 102.0; 161.9(3) C,Pt 80.6(3,5) 101.5; 162.3(3) I,Pt 60.4(1)	
(Me$_3$P)(η^1-SC$_6$H$_4$Me-4). Pt(μ-CO)(μ-tpm). Mn(CO)(η^5-cp) (dark orange)	or Pca2$_1$ 4	1948.2(4) 1282.7(4) 1164.9(2)		PtC$_2$SPMn	μOC 211.0(9) μC 213.2(8) ηS 236.5(3) P$_{Me}$ 231.9(2)	Mn 262.6(1) C 77.8(3) 82.6(4)	C,C 92.7(4) S,P 96.2(1) C,P 83.4(3) 168.6(3) S,P 96.2; 170.3(3) C,Mn 51.1(2,1.5) S,Mn 139.9(1) P,Mn 123.7(1)	134
				MnC$_8$Pt	OC 176(1) μOC 185.9(9) μC 204.7(9) C$_{cp}$ 215(1,2)		μC,μC 103.5(4) μC,Pt 52.7(2,1)	
[(Me$_3$P)$_2$Pt(μ-C- C$_6$H$_4$Me-4)Mn(CO)$_2$. (η^5-cp)]BF$_4$.CH$_2$Cl$_2$ (yellow)	m P2$_1$/c 4	1043.4(4) 1933.4(7) 1400.1(7)	94.42(4)	PtP$_2$CMn	P$_{Me}$ 227.4(2) 235.1(3) μC 196.7(8)	Mn 262.8(1) C 87.5(4)	P,P 97.6(1) P,C 100.3(2) 157.2(3) P,Mn 119.8(1) 142.5(1) C,Mn 44.1(2)	94
				MnC$_8$Pt	OC 181(1,1) C$_{cp}$ 215(1,2) μC 182.9(8)		μC,Pt 48.4(3)	
(MePh$_2$P)$_2$Pt(μ-CS). (μ-CO)Mn(CO)(η^5-cp) (yellow)	m P2$_1$/c 4	1665.5(4) 968.4(3) 2140.9(5)	114.57(2)	PtP$_2$CMn	P 230.8(2) 233.5(2) μC 201.5(8) μO 222.0(9)	Mn 264.1(1) C 83.4(3,2.0)	P,P 99.8(1) C,C 87.2(3) P,C 89.4(3,7.6) 160.0(3,1.2) P,Mn 130.1(1,6.2) C,Mn 43.8(2,1.5)	135
				MnC$_8$Pt	OC 177(1) μOC 179.8(8) μC 187.8(8) C$_{cp}$ 216.1(9,10)		μC,μC 105.4(4) μC,Pt 52.9(2,3.4)	
(cy$_3$P)(Et)Pt(μ-H). Re(H)$_3$(η^2-dbpe) (yellow)	m P2$_1$/n 4	1326.7(4) 1622.3(4) 2150.5(5)	107.89(2)	PtHCReP	μH not given C$_{Et}$ 207.3(11) P$_{cy}$ 221.5(3)	Re 264.3(1)	C,P 93.3(4) C,Re 130.9(4) P,Re 134.4(1)	136
				ReH$_4$P$_2$Pt	H not given μH not given ηP 236.5(3,6)		P,P 85.0(1)[c] P,Pt 135.0(1,8.4)	
[(Me$_3$P)$_2$Pt(μ-tpm). Mn(CO)$_2$(η^5-cp)]BF$_4$ (red)	tr $P\bar{1}$ 2	1037.7(2) 1023.0(2) 1391.7(4)	92.80(2) 95.28(2) 90.68(2)	PtP$_2$CMn	P$_{Me}$ 225.0(2) 232.1(2) μC 207.8(5)	Mn 264.5(1) C 78.4(2)	P,P 94.6(1) P,C 101.6(1) 163.1(1) P,Mn 112.8(1) 152.6(1)	134
				MnC$_8$Pt	OC 176.4(7,11) C$_{cp}$ 215.7(7,22) μC 210.7(5)		C,Mn 51.3(1) μC,Pt 50.3(1)	
(Me$_3$P)$_2$Pt(μ-ocp). Mn(CO)$_4$ (yellow)	tr $P\bar{1}$ 2	942.9(5) 1211.3(4) 972.9(6)	93.97(4) 115.45(4) 98.83(3)	PtP$_2$CMn	P$_{Me}$ 226.7(3) 229.3(4) μC 198(1)	Mn 265.8(2)	not given	137
				MnC$_6$Pt	OC not given μC 222(1) C 228(1)		not given	
(Me$_3$P)$_2$Pt(μ-ocp). Mn(CO)$_4$ (red)	m P2$_1$/n 4	935.8(5) 1288.4(9) 1598.9(9)	98.14(4)	PtP$_2$CMn	P$_{Me}$ 223.1(1) 226.7(3) μC 201.4(9)	Mn 269.3(1)	not given	137
				MnC$_6$Pt	OC not given μC 218(1) C 225.3(9)		not given	

Continued **Table 4.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Mn or Re)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
[(η^4-cod)Pt(μ-CPh). Re(CO)$_2$(η^5-cp)]BF$_4$ (orange)	m P2$_1$/n 4	1368.6(6) 827.9(4) 1959.4(9)	 100.40(1)	PtC$_5$Re	ηC 223.3(10,20) 230.9(9,1)	Re 270.69(13) C 88.3(4)	μC,Re 44.7(3)	138
				ReC$_7$Pt	μC 198.1(8) OC 194.6(11,5) C$_{cp}$ 227.5(11,27) μC 190.4(9)		C,C 88.1(4) C,μC 100.3(4,2.8) μC,Pt 47.0(2)	
(η^4-cod)Pt{μ-C(OMe)Ph}. Re(CO)$_2$(η^5-cp) (yellow)	m P2$_1$/c 4	1069.9(1) 1455.0(1) 1375.6(2)	 97.73(1)	PtC$_5$Re	ηC 220.5(4,7) 233.7(4,23) μC 205.5(4)	Re 271.88(3) C 80.15(13)	μC,Re 51.71(10)	138
				ReC$_7$Pt	OC 190.2(5,18) C$_{cp}$ 230.0(4,12) μC 216.6(4)		C,C 87.4(2) C,μC 101.8(1,3.3) μC,Pt 48.14(10)	
(Et$_3$P)$_2$Pt(μ-H). (μ-CO)Mn(CO)$_4$	m P2$_1$ 4	1114.2(2) 1899.9(4) 1166.1(2)	 104.81(1)	PtP$_2$HCMn	P$_{Et}$ 231.7(10) μH not given μOC 203(1)	Mn 272.8(6) H not given C 84(1)	P,μC 89.1(8) 164.1(9)	139
				MnC$_5$HPt			C,C 104.171(2) C,μC 91.164(1) μC,Pt 48(1)	
(Ph$_3$P)$_2$Pt(μ-CH$_2$). Re(CO)$_2$(η^5-cp) (burgundy) at 113K	or Pbca 8	1608.4(5) 2069.1(7) 2539.7(8)		PtP$_2$CRe	P$_{Ph}$ 226.1(2) 232.1(3) μC 204.8(9)	Re 273.0(1) C 81.5(4)	P,P 103.4(1) P,μC 95.1(2) 160.2(3) P,Re 110.1(1) 145.4(1) μC,Re 50.7(2)	140
				ReC$_8$Pt	OC 189.6(10,9) C$_{cp}$ 230.6(9,33) μC 213.5(9)		C,C 83.4(4) C,μC 84.3(4) 102.8(4) μC,Pt 50.7(2)	
(η^2-dppe)Pt(μ-C$_2$B$_9$H$_{10}$). Re(CO)$_3$ (orange yellow)	tr P$\bar{1}$ 2	1130.2(2) 1304.93(12) 1550.8(4)	66.198(14) 80.29(2) 66.735(10)	PtP$_2$BRe	ηP 220.2(4) 231.4(4) μB 206.1(18)	Re 275.83(9) B not given	P,P 86.9(2)[c] P,μB 97.0(4) 173.4(4) P,Re 122.29(10) 150.75(11) μB,Re 54.2(4)	141
				ReC$_5$B$_3$Pt	OC 192(2,3) μη^{5}C 230.2(14,6) μη^{5}B 238(2,1) μη^{5}B 228(2)		C,C 87.9(8,5.6) C,Pt 67.2(5) 80.5(3,1.1) μB,Pt 47.1(4)	
(Ph$_3$P)$_2$Pt(μ-CB$_{10}$H$_{11}$). Re(CO)$_3$ (yellow)	m C2/c 8	2346.1(3) 1210.1(2) 3100.4(6)	 109.243(12)	PtP$_2$HBRe	P$_{Ph}$ 229.50(8) 231.37(8) H 157(4) μB 235.5(3)	Re 279.31(4) B 74.56(11)	P,P 96.51(3) P,μB 109.03(9) 154.45(9) P,Re 103.39(2) 160.10(2) μB,Re 51.08(9)	142
				ReC$_4$B$_4$Pt	OC 195.7(4,16) μη^{5}C 231.5(3) μη^{5}B 232.8(3,21) μη^{5}B 225.4(4)		C,C 85.1(1,5) 110.23(13) C,Pt 75.07(9,45) 144.60(10)	
[(η^2-dppe)Pt(μ-C$_2$B$_9$H$_{10}$). Re(CO)$_3$]BF$_4$.CH$_2$Cl$_2$ (yellow)	tr P$\bar{1}$ 2	1212.2(3) 1308.4(2) 1515.5(3)	110.42(3) 106.75(2) 92.59(2)	PtP$_2$HBRe	ηP 226.0(4,8) H not given μB 234(2)	Re 281.26(10)	P,P 84.6(2)[c] P,B 115.2(6) 159.8(5) P,Re 108.42(12) 166.95(11) μB,Re 51.9(5)	141
				ReC$_5$B$_3$Pt	OC 194(2,2) μη^{5}C 235(2,1) μη^{5}B 234(2,1) μη^{5}μB 229(2)		C,C 82.1(9,8) 106.7(5,2.6) 143.1(5) μB,Pt 53.4(4)	
(Ph$_3$P)Pt{μ-η^2-F$_2$PN- (Me)PF$_2$}$_2$Re(CO)$_3$ (yellow)	m P2$_1$/m 2	1127.4(2) 1426.26(9) 1237.5(1)	 114.56(1)	PtP$_3$Re	P$_{Ph}$ 233.6(2) μη^{2}P 220.8(1,0)	Re 281.8(1)	P,P 96.88(4) 158.77(8) P,Re 86.13(4) 160.96(6)	143
				ReC$_3$P$_2$Pt	OC 192.5(9) 197.5(7,0) μη^{2}P 232.3(2,0)		C,C 93.2(6) P,P 97.62(8) C,Pt 89.3(2) 176.6(3) P,Pt 86.15(4)	

Continued **Table 4.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Mn or Re)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	Pt - M [pm] Pt – L - M [°]	L – M - L [°]	Ref.
$(Ph_3P)_2(H)Pt.Re(H)(CO)_2(\eta^5\text{-cp})$ (yellow)	not given			PtP_2HRe	H not given P_{Ph} 224.9(1) 233.6(1)	Re 283.8(1)	P,P 102.2(1) P,Re 108.2(1) 146.9(1)	144
				ReC_7HPt	OC 188.6(5,5) C_{cp} not given H not given		C,C 91.4(2) C,Pt 73.8(2) 109.4(2)	
$[ClPt(\mu\text{-CO})(\mu\text{-}\eta^2\text{-dppm})_2.Re(\eta^1\text{-}4\text{-MeC}_6H_4N_2)Cl].2Me_2CO)$ (yellow gold)	or $P2_12_12_1$ 4	1187.5(1) 1898.2(2) 2664.2(4)		PtP_2CClRe	μηP 230.5(6,2) μOC 220.8(17) Cl 240.8(6)	Re 285.9(4) C 87.4(7)	P,P 166.3(1) μC,Cl 138.1(4) Cl,Re 179.8(2) μC,Re 42.1(4)	145
				$ReP_2NCClPt$	μηP 243.1(6,1) ηN 178.6(14) μOC 191.8(17) Cl 244.1(6)		P,P 170.0(1) N,μC 101.0(7) N,Cl 120.7(5) μC,Pt 50.5(6)	
$[(Ph_3P)_2Pt(\mu\text{-H})(\mu\text{-PPh}_2).Re(NO)(\eta^5\text{-cp})]BF_4$ (yellow gold)	tr $P\bar{1}$ 2	1256.3(2) 1289.6(1) 1502.4(2)	94.14(1) 96.93(2) 92.01(1)	PtP_3HRe	P_{Ph} 226.9(2) 236.1(2) μH 221(6) μP 225.5(2)	Re 286.73(4) H not given P 77.21(7)	P,P 100.74(8) P,μP 102.75(8) P,Re 103.84(5) 154.75(6) μP,Re 52.73(1)	146 147
				ReC_5HNPPt	C_{cp} not given μH 157(6) ON 174.0(7) μP 234.0(2)		N,μP 91.9(3) N,Pt 100.0(2) μP,Pt 50.07(5)	
$[(Ph_3P)_2Pt(\mu\text{-Pcy}_2).Re(H)(NO)(\eta^5\text{-cp})].BF_4.CH_2Cl_2$ (yellow gold)	m $P2_1/n$ 4	1103.1(2) 2239.1(5) 2160.3(7)	94.04(2)	PtP_3Re	P_{Ph} 229.9(2) 235.1(2) μP 224.4(2)	Re 286.75(5) P 77.16(7)	P,P 101.56(8) P,μP 103.19(8) 155.22(8) P,Re 102.28(6) μP,Re 155.85(6)	147
				ReC_5HNPPt	C_{cp} not given H not given ON 174.1(9) μP 235.3(2)		N,μP 96.1(3) N,Pt 91.3(3) μP,Pt 49.71(5)	
$[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-dmpm})_2.Re(CO)_3]Br.H_2O$ (yellow orange)	m $P2_1/c$ 4	1222.4(2)] 973.7(1) 3198.6(5)	90.93(10	PtP_3Re	P_{Ph} 236.4(2) μηP 229.5(2,9)	Re 286.77(4)	P,P 95.72(8,45) 158.21(9) P,Re 87.66(6,2)	148
				ReC_3P_2Pt	OC 191(1,3) μηP 243.5(3,6)		C,C 90.2(5,3.1) P,P 95.62(9) C,Pt 91.2(3,1.1) 175.7(4) P,Pt 87.70(6,4.14)	
$[(Ph_3P)_2Pt(\mu\text{-Pcy}_2).Re(H)(NO)(\eta^5\text{-cp})].PF_6.2.5CH_2Cl_2$ (yellow gold)	tr $P\bar{1}$ 2	1253.2(2) 1307.7(2) 1910.1(2)	94.85(1) 105.0(1) 91.23(1)	PtP_3Re	P_{Ph} 225.6(4) 239.2(5) μP 228.5(5)	Re 288.15(8) P 76.8(2)	P,P 99.1(2) P,μP 103.2(2) 157.5(1) P,Re 105.35(9) 155.4(1) μP,Re 52.7(1)	147
				ReC_5HNPPt	C_{cp} not given H not given ON 173.6(15) μP 235.5(4)		N,P 94.6(5) N,Pt 96.5(5) μP,Pt 50.5(1)	
$[(Ph_3P)(Br)Pt(\mu\text{-}\eta^2\text{-F}_2PN\text{-}(Me)PF_2)_2Re(CO)_3].CH_2Cl_2$ (yellow)	m C2/m 4	1264.9(2) 1490.8(1) 1979.8(2)	96.600(9)	PtP_3BrRe	P_{Ph} 235.4(2) μηP 218.7(2,0) Br 273.8(1)	Re 289.88(5)	P,P 96.69(5) 145.08(3) P,Br 89.28(7) 106.13(7) P,Re 83.69(6) 178.64(6) Br,Re 89.36(3)	149
				ReC_3P_2Pt	OC 194(2,3) μηP 230.6(3,0)		C,C 88.5(5,1.8) P,P 95.0(1) C,P 87.2(4,0) C,Pt 86.8(3) 172.5(1) P,Pt 88.82(7)	

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 member metallocyclic ring.

by μ-H and μ-CO ligands with Pt-C-Mn bridge angle of 84(1)°, the hydrido bridge angle is not given.

In three yellow Pt/Re derivatives the Pt-Re bonds, 281.8(1) pm [143], 286.77(4) pm [148] and 289.88(5) pm [149] are spanned by a pair of μ-η²-$F_2PN(Me)PF_2$ [143,149] or a pair of μ-η²-dmpm ligands. In a Pt/Re complex [144] the $(Ph_3P)_2HPt$ and $Re(H)(CO)_2(\eta^5\text{-cp})$ fragments are held together by a direct Pt-Re bond of 283.8(1) pm length.

The structure of an orthorhombic Pt/Re compound is shown in Fig. 6. The Pt-Re bond of 285.9(4) pm is spanned by two μ-η²-dppm-P,P bridges to give an eight membered ReP_4C_2Pt ring in a boat conformation. The semi-bridging carbonyl group has a strong interaction with the Pt atom (Pt-C = 220.8(17) pm).

The data in Table 4 shows the shortest Pt-Re bond is 260.3(1) pm [133], while the mean Pt-Re bond length of 265.3 pm ranges from this value to 272.8(6) pm [139]. This is about 15.1 pm shorter than the mean Pt-Mn value of 280.4 (range 264.3(1) [143] to 289.88(5) pm [149]. The mean Pt-X-M bridge angle opens with decreasing covalent radius of the bridging atom X in the order: 58.2° (I, 133 pm) < 77.0° (P, 102 pm) < 83.1° (C, 77 pm).

There are three types of crystal class, monoclinic, triclinic and orthorhombic, with the former being most common with 13 examples. The derivative $(Me_3P)Pt(\mu$-ocp)$Mn(CO)_4$ exists in two isomeric forms [137], yellow monoclinic and red triclinic, differing mostly by degree of distortion and representing another example of distortion isomerism [76].

2.2.4 Fe and Ru

Forty eight coloured PtM derivatives of this type, 41 with M = Fe and 7 with M = Ru, are listed in Table 5. Several types of bridge are seen spanning the Pt-M bond. The most common of these, with fourteen examples [150-152,154,155,157,160,163] have one M-CL with one M-η^2-P,P' (most prevalent being μ-η^2-dppm-P,P') spanning the Pt-Fe bonds. The bonds range from 250.62(9) [150] to 269.81(8) pm [155] (av. 253.7 pm). The Pt-C-Fe bridge angles range from 76.8(5)° [157] to 82.7(2)° [155] (av. 79.9°). The next type involves a μ-PPh_2 [161,162,165,169,173,175] or μ-Pcy_2 [162,170] spanning the Pt-Fe bond. The bonds range from 262.0(1) [161] to 276.69(7) pm [175] (av. 268.6 pm). The Pt-P-Fe bridge angles range from 71.68(4)° [161] to 75.41(4)° [175] (av. 73.8°).There is only one example [153] where μ-CL is replaced by μ-I, with a Pt-Fe bond distance of 252.3(4) pm and Pt-I-Fe angle of 57.1°.

In another five Pt-M examples (M = Fe [156] or Ru [167,168]) the Pt-M bonds are spanned by a μ-C ligand. The Pt-M bond lengths are: Pt-Fe 256.9(1) pm [156], Pt-Ru 266.4(1) and 270.09(8) pm [167], 266.8(1) and 271.8(1) pm [168].

There are two yellow Pt-Fe derivatives [158,159] with similar structures, of which one is shown in Fig. 7. The four membered Fe-Si-O-Pt rings and five membered Fe-P-C-P-Pt ring are almost coplanar. The Pt-Fe bond distance of 258.18(8) pm [158] is about 12.1 pm shorter than that of the other [159]. Differences can also be seen in other bond distances, for example: Pt-O 213(1) pm [158] *vs.* 221.7(4) pm [159]; Pt-P 220.6(2) *vs.* 217.1(2) pm. Also bond angles differ for O-Pt-Fe and P-Pt-Fe, with values of 80.4(2)° and 94.6(1)° in the former, 77.3(1)° and 93.17(5)° in the latter.

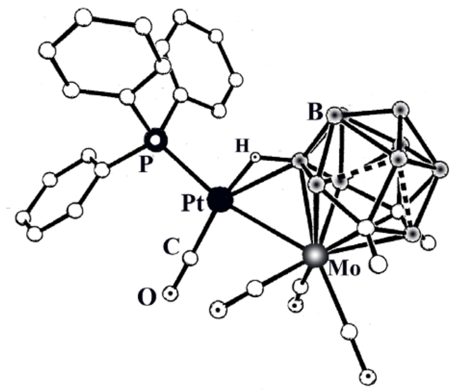

Figure 5. Structure of $[(Ph_3P(OC)Pt(\mu$-η^6-$C_2B_{10}H_{10}Me_2)Mo(CO)_3]$ [114]

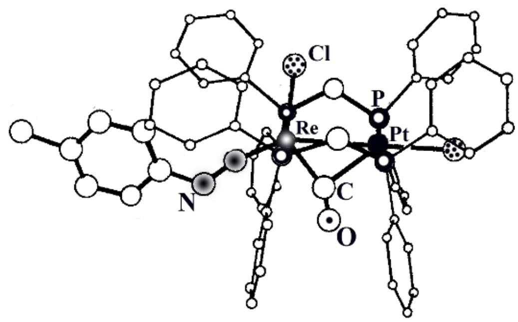

Figure 6. Structure of $[ClPt(\mu$-CO$)(\mu$-η^2-dppm$)_2$Re$(\eta^1$-4-Me$C_6H_4N_2)$Cl] [145]

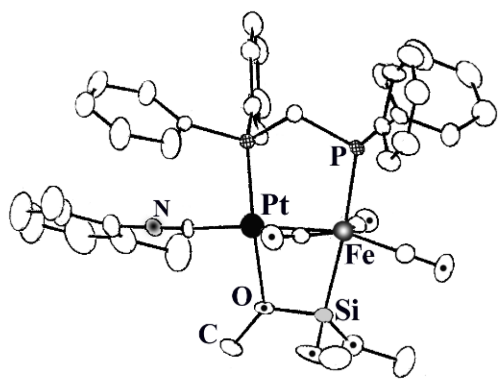

Figure 7. Structure of [(2,6-xylylNC)Pt(μ-η^2-O(Me)Si(OMe)$_2$}{μ-η^2-dppm)Fe$(CO)_3^+$ [158]

Two Pt/Fe derivatives [164,172] have the Pt and Fe moieties held together only by the Pt-Fe bond, with distances of 265.69(13) and 268.5(1) pm, respectively.

There are five Pt/Fe derivatives with Pt-Fe bonds of 266.1(1) [166], 267.0(2) [152], 267.5(3) [171], 269.40(8) [159] and 279.8(2) pm [154]. These are spanned by μ-η^2-dppm-P,P' [154,159,166,171] or μ-η^2-dppa-P,P' [152], creating a five membered ring Pt-P-X-P-Fe where X= C or N.

Table 5. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
[(Ph_3P)Pt{μ-C(Et)OSi-($OMe)_3$}(μ-η²-dppm).Fe($CO)_3$].2tol (yellow) at 173K	m $P2_1/c$ 4	1101.4(1) 2114.8(1) 2606.3(1)	 94.57(2)	PtP_2CFe	P_{Ph}[b] 226.0(2) μη²P 231.1(2) μC 207.4(7)	Fe 250.62(9) C not given	P,P[b] 106.74(6) P,μC 104.8(2) 148.1(2) P,Fe 95.62(5) 157.27(5) μC,Fe 52.6(2)	150
				FeC_4PPt	OC 178.1(7,5) μC 206.6(7) μη²P 223.0(2)		C,Pt 77.8(2,4.4) 154.2(2) μC,Pt 52.9(2) P,Pt 99.54(6)	
(Ph_3P)Pt{μ-CN(Me)2,6-xylyl}(μ-η²-dppa)Fe($CO)_3$ (yellow)	m $P2_1/c$ 4	1102.6(6) 1852.4(9) 2370.8(12)	 90.49(4)	PtP_2CFe	P_{Ph} 227.7(1) μηP 234.9(2) μC 199.6(5)	Fe 251.7(1) C 80.0(2)	P,P 108.97(5) P,μC 109.5(1) 141.40(13) P,Fe 157.14(4) μC,Fe 48.6(1)	151
				FeC_4PPt	OC not given μC 191.8(4) μηP 227.6(2)		μC,Pt 51.3(2) P,Pt 95.60(5)	
(Ph_3P)Pt{μ-CN(2;6-xylyl)}(μ-η²-dppm).2Fe($CO)_3$ (orange)	tr $P\bar{1}$ 2	1208(2) 1354(3) 1860(3)	101.86(14) 100.72(13) 111.81(12)	PtP_2CFe	P_{Ph} 224.3(3) μηP 229.7(5) μC 199.4(8)	Fe 252.2(4) C 78.6(3)	P,P 106.4(2) P,μC 105.7(3) 147.7(2) P,Fe 155.94(9) μC,Fe 50.6(2)	152
				FeC_4PPt	OC 176.5(9,4) 183.6(11) μC 198.8(8) μηP 212.12(5)		μC,P 147.7(3) μC,Fe 50.8(2)	
(Ph_3P)Pt{μ-CN(σ-anisyl)}.(μ-η²-dppm)Fe($CO)_3$ (orange)	m $P2_1/n$ 4	1872.7(4) 1266.8(3) 2070.6(4)	 109.19(3)	PtP_2CFe	P_{Ph} 225.9(3) μηP 231.3(3) μC 201.3(10)	Fe 252.2(2) C 79.2(4)	P,P 109.61(10) P,μC 102.0(3) 148.4(2) P,Fe 151.48(8) μC,Fe 50.0(3)	152
				FeC_4PPt	OC 177.9(14,10) μC 199.1(10) μHP 222.6(3)		μC,P 143.4(3) μC,Fe 50.8(3)	
[(I)Pt(μ-I)(μη²-dppm).Fe($CO)_3$].CH_2Cl_2 (dark brown)	m $P2_1/c$ 4	991.3(2) 1398.7(3) 2356.8(4)	 95.96(1)	PtI_2PFe	I 265.6 μI 266.4 μηP 219.5(3)	Fe 252.3(4) I 57.1	I,μI 102.7 I,P 100.2 μI,P 156.7 I,Fe 162.7 μI,Fe 60.5 P,Fe 96.3	153
				FeC_3PIPt	OC 180.7(8,27) μηP 220.2(3) μI 261.6(4)		P,Pt 98.2 μI,Pt 62.4	
[(Ph_3P)Pt{μ-CN(Me)σ-anisyl}(μ-η²-dppa).Fe($CO)_3$].CF_3SO_3 (yellow)	tr $P\bar{1}$ 2	1310.5(3) 1438.7(3) 1499.7(7)	81.29(3) 71.77(3) 78.09(3)	PtP_2CFe	P_{Ph} 229.1(1) μηP 232.7(2) μC 192.3(5)	Fe 252.8(1) C 80.9(2)	P,P 112.18(5) P,μC 103.5(2) 144.2(2) P,Fe 151.32(4) μC,Fe 48.7(2) P,μC 146.9(2)	151
				FeC_4PPt	OC not given μC 197.5(6) μη²P 222.6(3)		P,Pt 96.45(5) μC,Pt 50.5(2)	
[(Ph_3P)Pt{μ-C=C(H)Ph}.(μ-η²-dppm)Fe($CO)_3$].0.5CH_2Cl_2 (yellow)	tr $P\bar{1}$ 2	1238.8(2) 1311.4(2) 1631.5(2)	107.260(9) 93.790(9) 103.420(9)	PtP_2CFe	P_{Ph} 227.0(2) μηP 231.9(2) μC 199.8(6)	Fe 255.03(8) C 79.0(2)	P,P 104.52(5) P,μC 105.6(2) 149.8(2) P,Fe 98.90(4) 156.06(5) μC,Fe 50.3(2)	154
				FeC_4PPt	OC 178.5(7,25) μC 201.9(6) μηP 223.3(2)		μC,P 142.5(2) P,Pt 93.19(5)	
[(Ph_3P)Pt{μ-CNbz}.(μ-η²-dppm)Fe($CO)_3$].0.5CH_2Cl_2 (orange)	tr $P\bar{1}$ 2	1171.3(2) 1277.9(3) 1879.8(4)	107.03(3) 92.26(3) 113.18(3)	PtP_2CFe	P_{Ph} 226.32(13) μηP 230.87(13) μC 198.4(5)	Fe 255.77(10) C 78.9(2)	P,P 107.17(5) P,μC 102.70(14) 148.99(14) P,Fe 154.18(4) μC,Fe 51.51(14)	155
				FeC_4PPt	OC 177.9(5,17) μC 204.0(5) μηP 224.0(2)		μC,P 144.08(13) μC,Pt 49.58(12) P,Pt 93.63(8)	

Continued **Table 5.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(Ph_3P)_2Pt(\mu-CH_2)Fe(CO)_4$ (yellow)	m $P2_1/c$ 4	1033.8(2) 1960.4(5) 1842.2(4)	105.30(2)	PtP_2CFe	P_{Ph} 225.9(2) 230.8(2) μC 205.4(8)	Fe 256.9(1) C 77.4(3)	P,P 106.2(1) P,μC 92.3(2) 161.4(2) P,Fe 110.0(1) 143.3(1) μC,Fe 51.3(2)	156
				FeC_5Pt	OC 179.5(11,19) μC 205.6(8)		μC,Pt 51.3(2)	
$[(Ph_3P)Pt(\mu-CO)(\mu-\eta^2-dppm)Fe(CO)_3].C_6H_6$ (orange)	tr $P\bar{1}$ 2	1177.3(2) 1198.4(1) 1776.5(1)	103.34(1) 107.81(1) 91.76(1)	PtP_2CFe	P_{Ph} 226.9(3) μηP 234.7(3) μOC 199.2(7)	Fe 257.9(4) C 80.2(3)	P,P 115.6 P,μC 100.2(2) 144.2(1) P,Fe 94.3; 148.3 μC,Fe 50.3(2)	157
				FeC_4PPt	OC 176.5(8,24) μOC 201.2(7) μηP 225.2(3)		μC,Pt 49.6(1) P,Pt 97.8	
$[(2,6-xylylNC)Pt\{\mu-\eta^2-O(Me)Si(OMe)_2\}(\mu-\eta^2-dppm)Fe(CO)_3].PF_6$ (yellow)	tr $P\bar{1}$ 2	1084.3(3) 1115.6(6) 2002.2(4)	93.47(3) 98.66(3) 95.66(3)	PtOCPFe	μηO 213(1) RNC 197.7(6) μηP 220.6(5)	Fe 258.18(8)	O,C 93.8(2) O,P 174.4(3) C,P 91.5(2) O,Fe 80.4(2) C,Fe 171.0(1) P,Fe 94.6(1)	158
				FeC_3PSiPt	OC 177(2,1) μηP 222(2) μηSi 226.3(2)		P,Si 174.0(4) P,Pt 98.0(4) Si,Pt 76.01(4)	
$(\eta^4-cod)Pt(\mu-PPh_2).Fe(CO)_3\{Si(OMe)_3\}$ (yellow)	m $P2_1/c$ 4	920.4(1) 1568.9(1) 1960.0(1)	93.46(2)	PtC_4PFe	η^4C 221.0(6,14) 230.4(6,16) μP 223.9(1)	Fe 259.40(7) P 71.69(4)	C,μP 108.9(2,2.1) 155.7(2) C,Fe 111.0(2,2.8) 155.3(2,5) μP,Fe 53.30(4)	159
				FeC_3PSiPt	OC 177.2(6,4) μP 219.2(1) Si 229.6(2)		C,μP 97.1(2,2.5) C,Si 80.6(2,3) 93.9(2) P,Pt 55.01(4)	
$(Ph_3P)Pt\{\mu-C(O)C_2H_2-\eta^4\}.(\mu-\eta^2-dppm)Fe(CO)_2$ (orange)	or Pbca 8	1898.9(4) 1828.3(3) 2414.4(5)		PtP_2CFe	P_{Ph} 226.8(4) μηP 227.7(4) μC 202.2(9)	Fe 259.7(4) C 77.8(4)	P,P 106.3(2) P,μC 98.8(3) 152.5(2) P,Fe 101.6(2) 151.5(2) μP,Fe 52.7(3)	157
				FeC_5PPt	OC 175.4(10,10) C 191.3(9) 209.5(9) μC 211.4(9) μηP 220.5(4)		μC,P 137.9(2) μC,Pt 49.5(2) P,Pt 88.5(2)	
$(Ph_3P)Pt\{\mu-C(CMe_2)CH_2-\eta^4\}(\mu-\eta^2-dppm)Fe(CO)_2$	m $P2_1/c$ 4	1098.4(3) 1889.8(6) 2216.3(5)	103.52(2)	PtP_2CFe	P_{Ph} 226.4(3) μηP 227.4(3) μC 204.1(7)	Fe 261.8(4) C 81.5(3)	P,μP 102.5(2) P,Fe 150.5 μC,Fe 48.1(1) μC,Pt 50.4(3)	160
				FeC_5PPt	OC 176.1(9,5) μηC 217.8(8,34) μC 197.1(7) μηP 218.9(4)			
$(Ph_3P)(OC)Pt(\mu-PPh_2).Fe(CO)_3(SiPh_3)$ (yellow)	m $P2_1/c$ 4	1250.4(5) 1973.9(4) 1857.8(9)	103.95(2)	PtP_2CFe	P_{Ph} 229.4(1) μP 227.7(1) OC 191.6(6)	Fe 262.0(1) P 71.68(4)	P,μP 105.02(5) P,C 100.4(2) μP,C 154.3(2) P,Fe 155.93(4) μP,Fe 52.72(4) C,Fe 101.6(2)	161
				FeC_3PSiPt	OC 177.6(6,20) μP 219.6(2) Si 233.9(2)		μP,Si 177.96(6) μP,Pt 55.61(4) Si,Pt 126.12(5)	
$[(Ph_3P)Pt(\mu-C(Me)=CH_2-\eta^3\}.(\mu-\eta^2-dppm)Fe(CO)_3].BF_4$ (yellow)	m Cc 4	2321.3(3) 1091.2(2) 1962.6(2)	98.48(1)	PtP_2CFe	P_{Ph} 225.0(6) μηP 240.7(5) μC 202.5(14)	Fe 263.0(5) C 76.8(5)	P,P 107.0(2) P,μC 105.6(2) 146.5(4) P,Fe 94.0(2) 158.3(1) μC,Fe 54.6(5)	157
				FeC_5PPt	OC 177.5(17,37) C 223.5(16) μC 220.1(15) μηP 231.0(6)		μC,P 139.5(3) μC,Pt 48.6(3) P,Pt 96.6(2)	

Continued **Table 5.** Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
(Ph_3P)(xylylNC)Pt. (μ-PPh_2)$Fe(CO)_3(SiPh_3)$ (yellow)	m $P2_1/n$ 4	1202.7(5) 1817.9(4) 2382.0(9)	 98.01(3)	PtP_2CFe	P_{Ph} 227.8(2) RNC 196.2(9) μP 226.2(2)	Fe 263.1(1) P 72.24(7)	P,μP 107.78(8) P,C 97.6(3) μP,C 154.4(3) μP,Fe 159.88(6) C,Fe 101.78(8)	162
				FeC_3PSiPt	OC 177(1,1) μP 220.0(2) Si 233.1(2)		P,Si 175.0(1) P,Pt 54.96(6) Si,Pt 129.55(8)	
(Ph_3P)Pt{μ-η²-C(=CH_2)CH_2}. (μ-η²-dppm)$Fe(CO)_3$ (yellow)	m $P2_1/n$ 4	1195.1(2) 2258.5(3) 1673.9(4)	 108.15(2)	PtP_2CFe	P_{Ph} 232.8(3) μηP 232.6(3) μηC 209.3(8)	Fe 263.4(4)	P,P 104.1 P,C 89.7(3) 166.1(3) P,Fe 92.6 162.9 C,Fe 73.7(3)	157 160
				FeC_4PPt	OC 180.4(8,19) μηC 208.8(7) μηP 224.3(3)		C,P 170.9(2) C,Pt 72.9(3) P,Pt 100.9	
Br_2Pt(μ-CO)(μ-η²-dppm). $Fe(CO)_3$ (yellow-orange)	m $P2_1/n$ 4	1256.9(2) 1780.6(2) 1343.6(1)	 102.35(1)	$PtBr_2CPPt$	Br 247.6(3,1) μOC 221.1(8) μηP 224.0(3)	Fe 264.7(4) C 80.8(3)	Br,Br 163.9 μC,P 91.5(2) Br,μC 93.6(2,2.1) Br,P 86.7; 172.6 Br,Fe 89.7; 163.9 μC,Fe 43.6(2) P,Fe 96.6	153 163
				FeC_4PPt	OC 180.9(9,37) μOC 185.0(9) μηP 227.1(4)		μC,P 91.9(3) μC,Pt 55.6(3) P,Pt 94.3	
(η³-C_8H_{12}-cp)$PtFe(CO)_3$ (η³-C_7H_7) (red brown)	m C2/c 8	4519.7(6) 1330.6(1) 750.9(1)	 92.96(1)	PtC_3Fe	ηC 209.8(9) 217.0(9,6)	Fe 265.69(13)	not given	164
				FeC_6Pt	OC 178.3(12,12) ηC 203.9(10) 218.6(10,8)		C,Pt 66.2(3) 81.8(3) 160.8(3)	
(η²-dppv)Pt(μ-PPh_2). $Fe(CO)_3(SiPh_3)$ (yellow)	tr $P\bar{1}$ 2	1213.1(5) 1233.4(5) 2020.9(6)	94.03(3) 95.81(4) 110.18(3)	PtP_3Fe	ηP 225.3(3) 232.1(3) μP 226.3(3)	Fe 265.9(2) P 73.2(1)	P,P 74.6(1)[c] P,μP 114.2(1) 171.2(1) P,Fe 118.99(8) 160.09(8) μP,Fe 52.28(8)	165
				FeC_3PSiPt	OC 176(1,3) μP 219.7(3) Si 235.6(3)		P,Si 175.3(1) μP,Pt 54.5(1) Si,Pt 129.9(1)	
[(Ph_3P)(H)Pt(μ-η²-dppm). $Fe(CO)_3(SiF_3)$].0.5C_6H_6 (yellow)	tr $P\bar{1}$ 2	1769.2(7) 1308.4(5) 1103.1(5)	112.16(1) 91.31(2) 101.71(1)	PtP_2HFe	P_{Ph} 222.5(2) μηP 231.8(2) H 171(8)	Fe 266.1(1)	P,P 103.9(1) P,H 80(3) P,Fe 94.9(1) H,Fe 81(3)	166
				FeC_3P_2Pt	OC 176.6(9,10) μηP 224.2(3) Si 224.9(3)		C,P 93.6(3,1.6) C,Si 86.2(3,2.6) Si,P 175.8(1) P,Pt 94.3(1) Si,Pt 88.2(1)	
(Ph_3P)(Bu^{t}NC)Pt. (μ-η¹;η²-tsc)Ru(CO)(η⁵-cp) (yellow)	m $P2_1/n$ 4	1150.2(3) 1651.8(4) 2300.8(5)	 102.50(2)	PtC_2PRu	RNC 196.4(13) μC 198.3(9) P_{Ph} 227(3)	Ru 266.4(1) C 80.1(4)	C,μC 152.8(4) C,P 100.3(3) μC,P 106.7(3) C,Ru 100.3(3) μC,Ru 52.8(3) P,Ru 159.34(7)	167
				RuC_8Pt	OC 183.6(12) μηC 215.0(9) μηC 215.3(10)		C,μC 39.3(3) μC,Pt 47.1(2)	
(Ph_3P)(OC)Pt. {μ-η¹;η²-C(Ph)=C=CH_2}. Ru(CO)(η⁵-cp) (red)	tr $P\bar{1}$ 2	1118.6(3) 1199.2(3) 1355.1(3)	100.74(2) 108.78(2) 112.03(2)	PtC_2PRu	OC 188.2(10) μC 202.5(9) P_{Ph} 229.3(2)	Ru 266.8(1) C not given	C,μC 160.1(4) C,P 97.8(3) μC,P 101.7(3) C,Ru 108.3(3) μC,Ru 52.7(3) P,Ru 153.4(1)	168
				RuC_8Pt	OC 184.4(12) ηC_{cp} not given μηC 210.7(8) μημC 216.2(9)		C,C 80.5(4) C,μC 100.8(4) μC,Pt 48.2(2) C,Pt 75.8(3,2.1)	

Continued Table 5. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(Ph_3P)(H)Pt(\mu-\eta^2-dppa).Fe(CO)_3\{Si(OMe)_3\}$ (colourless)	m $P2_1/n$ 4	1006.9(9) 1847.5(10) 2471(2)	 101.12(6)	PtP_2HFe	P_{Ph} 222.8(2) $\mu\eta P$ 230.4(2) H not given	Fe 267.0(2)	P,P 105.60(6) P,H 79.8(13) P,Fe 93.86(6) 157.68(3) H,Fe 80.5(13)	152
				FeC_3PSiPt	OC 175.3(4,7) $\mu\eta P$ 220.3(2) Si 229.8(2)		C,P 94.7(1,7.0) C,Si 84.0(1,3.9) P,Pt 91.61(6)	
$(NMe_4)[\eta^2-dppot)Pt(\mu-PPh_2)Fe\{Si(OMe)_3\}]$ (yellow)	tr $P\bar{1}$ 2	1153.6(1) 1166.2(1) 1721.9(1)	105.36(2) 101.18(2) 90.67(2)	PtP_2OFe	ηP 223.9(2) μO 211.4(5) μP 220.3(2)	Fe 267.2(1) P 74.39(6)	P,μP 115.71(8) P,O 82.8(1)[e] μP,O 161.5(1) P,Fe 168.23(6) μP,Fe 53.06(6) O,Fe 108.5(1)	169
				FeC_3PSiPt	OC 175(1,3) μP 221.8(2) Si 226.3(3)		μP,Fe 52.55(6) Si,Fe 120.94(9)	
$(Et_3P)_2Pt(\mu-Pcy_2)Fe(CO)_3Cl$ (orange)	tr $P\bar{1}$ 2	1003.7(4) 1064.4(3) 1713.7(9)	102.80(3) 76.74(3) 103.99(3)	PtP_3Fe	P_{Ph} 227.6(2) 233.0(1) μP 227.6(1)	Fe 267.3(1) P 73.4(1)	P,P 102.3(1) P,μP 107.0(1) 150.0(1) P,Fe 99.9(1) 157.1(1) μP,Fe 52.0(1)	170
				FeC_3ClPPt	OC 179.4(6,20) Cl 237.6(2) μP 219.9(2)		Cl,P 167.1(1) Cl,Pt 112.4(1) μP,Pt 54.6(1)	
$(\eta^3-C_3H_5)Pt(\mu-\eta^2-dppm).Fe(CO)_3\{Si(OSiMe_3)_3\}$ (colourless)	m $P2_1/n$ 4	1047.2(4) 1642.1(5) 2765.4(7)	 94.52(2)	PtC_3PFe	ηC 216.5(7,15) 227.9(9) $\mu\eta P$ 224.0(4)	Fe 267.5(3)	P,Fe 94.2(1)	171
				FeC_3PSiPt	OC 172.3(11) 178.6(13,3) $\mu\eta P$ 223.9(4) Si 232.4(4)		P,Pt 91.7(1) Si,Pt 98.5(1) C,Pt 71.8(4,4.5)	
$[(\eta^2-dppe)(Me)Pt.Fe(CO)_2(\eta^5-cp)].thf$	tr $P\bar{1}$ 2	1216.6(6) 1800.2(14) 945.1(4)	97.64(7) 101.70(4) 114.82(5)	PtP_2CFe	ηP 222.7(2) 228.2(2) C_{Me} 215.4(8)	Fe 268.5(1)	P,P 85.92(7)[e] P,C 88.5(3) P,Fe 95.35(6) C,Fe 90.2(3)	172
				FeC_7Pt	OC 175(1,1) ηC_{cp} 210(1,5)		C,Pt 74.4(3) 97.9(3)	
$(\eta^3-C_8H_{11})Pt(\mu-\eta^2-dppm).Fe(CO)_3\{Si(OMe)_3\}$ (yellow)	tr $P\bar{1}$ 2	1121.7(3) 1266.1(3) 1614.6(4)	83.73(2) 89.81(2) 64.54(2)	PtC_3PFe	ηC 213.2(6) 225.0(6,45) $\mu\eta P$ 223.6(1)	Fe 269.40(8)	C,C 37.3(3,6)[d] 66.5(2) C,P 97.4(2) 133.2, 159.4(2) P,Fe 94.22(4)	159
				FeC_3PSiPt	OC 175.7(6,8) $\mu\eta P$ 222.1(2) Si 229.4(2)		P,Pt 94.39(4) Si,Pt 92.73(5)	
$[(C_6H_{11}NC)(I)Pt(\mu-CO).(\mu-\eta^2-dppm)Fe(CO)_2(I)].CH_2Cl_2$ (red-violet)	m $P2_1/c$ 4	1523.6(3) 1178.1(3) 2243.0(5)	 98.17(3)	PtC_2PIFe	RNC 198.0(5) μOC 225.0(5) $\mu\eta P$ 228.91(12) I 265.53(6)	Fe 269.81(8) C 82.7(2)	C,P 174.74(13) C,Fe 93.59(14) P,I 90.50(4) I,Fe 168.95(2) P,Fe 91.44(4)	155
				FeC_3PIPt	OC 178.4(6,29) μOC 180.0(4) $\mu\eta P$ 227.12(13) I 266.0(5)		P,I 87.42(4) P,Pt 96.63(4) I,Pt 85.40(3)	
$(Ph_3P)_2Pt(\mu-PPh_2).Fe(H)(CO)_3$	m $P2_1/c$ 4	1055.1(2) 1904.9(3) 2409.2(4)	 98.29(1)	PtP_3Fe	P_{Ph} 226.9(3) 232.3(3) μP 224.7(3)	Fe 269.8(2) P not given	P,Fe 99.3 155.6 μP,Fe 51.0	173
				FeC_3HPPt	OC not given H not given μP 216.7(4)		C,Pt 97.5(-,2.6) 150.9 μP,Pt 53.7	
$[(Et_3P)_2Pt\{\mu-\eta^1;\eta^2-tsap).Ru(CO)(\eta^5-cp)]C_3H_6O$	tr $P\bar{1}$ 2	1079.7(6) 1205.0(10) 2280.9(20)	78.64(5) 89.72(5) 86.82(5)	PtP_2CRu	P_{Et} 226.0(2) 229.6(2) μC 202.8(9)	Ru 2700.9(8) C not given	P,P 102.15(8) P,μC 98.0(3) 159.2(3) μC,Ru 51.6(2)	167
				RuC_8Pt	OC 185.4(11) ηC 205.3(9) μC 214.7(9) ηC_{cp} not given		μC,Pt 47.8(2)	

Continued Table 5. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(Me_3P)_2Pt(\mu\text{-}PPh_2).$ **$Fe(CO)_3(SiPh_3)$** **(yellow)**	tr_ P1 2	1186.6(2) 1108.2(2) 2049.3(4)	96.84(1) 100.72(1) 113.90(0)	PtP_3Fe FeC_3PSiPt	P_{Me} 224.8(1) 230.6(1) μP 225.5(1) OC 176.7(6,17) μP 220.6(1) Si 233.0(2)	Fe 270.2(1) P 74.54(5)	P,P 97.45(5) P,μP 105.15(5) 157.39(5) P,Fe 105.49(4) 157.05(4) μP,Fe 51.90(4) μP,Si 170.31(6) μP,Pt 53.56(4) Si,Pt 135.83(4)	165
(η[1]-nbn)Pt{μ-η[2]-O(Me). **$Si(OMe)_2$}(μ-dppm).** **$Fe(CO)_3$** **(yellow)** **at 173K**	m $P2_1/n$ 4	1180.0(3) 2024.5(6) 1632.7(4)	 105.43(2)	PtOCPFe FeC_3PSiPt	μηO 221.7(4) ηC 205(2) μηP 217.1(2) OC 175.5(7,6) μηP 221.2(2) Si 224.3(2)	Fe 270.32(9)	O,C 90.4(4) O,P 170.5(1) C,P 98.8(4) O,Fe 77.3(1) P,Fe 93.17(5) C,P 95.0(2,5.7) C,Si 85.8(2,3.7) P,Si 172.10(8)	159
$[(Ph_3Si)(OC)Pt(\mu\text{-}PPh_2).$ **$Fe(CO)_4].0.5C_6H_{12}$** **(orange)**	m C_2/c 4	3574(1) 982.7(2) 2007.6(6)	 93.69(2)	PtCPSiFe FeC_4PPt	OC 189.9(7) μP 225.1(2) Si 236.4(2) OC 178.9(8,5) μP 227.5(2)	Fe 271.76(9) P 73.8(5)	C,μP 163.4(2) C,Si 90.7(2) μP,Si 105.17(6) Si,Fe 157.98(5) μP,Fe 53.50(4) C,P 102.6(3) 149.1(2) μP,Pt 52.69(4)	162
$(Ph_3P)_2Pt${μ-η[1];η[2]- **$CH{=}C{=}CH_2$}.** **Ru(CO)(η[5]-cp)** **(orange)**	tr_ P1 2	1121.0(2) 1272.6(3) 1398.4(2)	101.90(2) 101.74(2) 99.43(2)	PtP_2CRu RuC_8Pt	P_{Ph} 225.5(2) 230.2(2) μC 201.5(6) OC 183.8(6) μηC 209.8(7) μημC 211.6(6) ηC_{cp} not given	Ru 271.8(1) C not given	P,P 107.4(1) P,μC 94.6(2) 156.8(2) P,Ru 109.2(1) 142.9(1) μC,Ru 50.5(2) C,μC 98.2(3) C,Pt 75.8(2,7) μC,Pt 47.3(2)	168
$(Ph_3Si)(Bu^tNC)Pt(\mu\text{-}PPh_2).$ **$Fe(CO)_3(CNBu^t)$** **(orange)**	m $P2_1/c$ 4	1701.8(6) 1064.2(3) 2354.9(3)	 94.07(4)	PtCPSiFe FeC_4PPt	RNC 195.7(9) μP 223.3(2) Si 233.3(2) OC 176(1,2) RNC 189(1) μP 225.2(2)	Fe 271.9(1) P 74.64(7)	C,μP 157.7(2) μP,Si 112.90(7) μP,Fe 53.00(6) C,μP 104.6(4) μP,Pt 52.36(6)	162
$\{(MeO)_3Si\}(OC).$ **$Pt(\mu\text{-}Pcy_2)Fe(CO)_4$** **(orange)**	tr_ P1 2	1054.2(3) 1085.9(3) 1224.293)	100.15(2) 103.56(2) 94.98(2)	PtCPSiFe FeC_4PPt	OC 189.8(6) μP 225.9(1) Si 231.9(2) OC 179.5(6,23) μP 230.4(1)	Fe 272.33(7) P 73.28(3)	C,μP 167.3(2) C,Si 92.7(2) P,Si 98.07(5) P,Fe 54.13(3) Si,Fe 152.20(5) C,μP 89.9(2) 173.8(2) μP,Pt 52.59(3)	162
$(Ph_3P)_2Pt(\mu\text{-}H)${μ-CHC(O)-** **Me}Ru(CO)(η[5]-cp)** **(yellow)**	m $P2_1/n$ 4	1820.0(3) 1016.0(2) 2397.2(3)	 102.927(14)	PtP_2HCRu RuC_7Pt	P_{Ph} 225.4(2) 232.1(3) μH not given μC 203.2(10) OC 181.8(13) μC 209.9(8) ηC_{cp} not given	Ru 274.8(1) H not given C 83.4(3)	P,P 101.6(1) P,μC 96.0(2) 162.1(2) P,Ru 112.8(1) 145.2(1) μC,Ru 49.4(2) C,μC 91.9(4) C,Pt 95.3(4) μC,Pt 47.3(3)	174
$(Ph_3P)\{(MeO)_3Si\}.$ **$Pt(\mu\text{-}PPh_2)Fe(CO)_4$** **(yellow)**	not given			PtP_2SiFe FeC_4PPt	P_{Ph} 229.3(1) μP 225.0(1) Si 228.8(1) OC 179.3(6,17) μP 227.4(1)	Fe 276.69(7) P 75.41(4)	P,μP 165.60(4) P,Si 96.28(5) μP,Si 98.00(5) P,Fe 112.94(3) μP,Fe 52.69(3) Si,Fe 150.51(4) μC,Pt 51.91(3)	175
$[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-}dmpm)_2.$ **$Ru(\eta^5\text{-}cp)].PF_6.CH_2Cl_2$** **(dark red)**	or $P2_12_12_1$ 4	1105.4(1) 1837.9(2) 2124.9(4)		PtP_3Ru RuC_5P_2Pt	P_{Ph} 232.4(4) μηP 226.7(4) 231.5(4) ηc_{CP} 221(2,2) μηp 224.4(4,4)	Ru 276.9(1)	P,P 96.8(1,1.8) 161.8(2) P,Ru 84.8(1,1.7) 166.78(9) P,P 93.6(2) P,Fe 83.3(1) 96.6(1)	176

Continued Table 5. Heterobinuclear Platinum Compounds with Pt-M Bond (M = Fe or Ru)[a]

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
(MeCO)(Bu^{t}NC)Pt(μ-η^2-dppm)Fe(CO)$_3${Si(OMe)$_3$} (yellow)	m P2$_1$/n 4	1108(2) 1866.5(13) 2022(2)	 99.71(9)	PtC$_2$PFe	RNC 198.9(8) MeOC 205.6(8) μηP 227.3(3)	Fe 279.8(2)	C,C 84.5(3) C,P 86.3(2) 164.5(2) C,Fe 98.0(2) 172.1(2) P,Fe 92.77(6)	154
				FeC$_3$PSiPt	OC 176.0(8,15) μηP 222.4(3) Si 229.6(3)		P,Si 171.62(6) P,Pt 92.33(7) Si,Pt 94.77(7) P,Pt 92.33(7) Si,Pt 94.77(7)	
(Et$_3$P)$_2$Pt(μ-H)(μ-Pcy$_2$). Fe(CO)$_3$ (yellow)	m P2$_1$/c 4	1001.0(8) 2469.5(13) 1415.2(12)	 108.50(7)	PtP$_3$HFe	P$_{Et}$ 229.5(7) 232.1(7) μP 231.1(7) μH not given	Fe 280.0(4) H not given P not given	P,Fe 107.0 153.2 μP,Fe 49.9	173
				FeC$_3$HPPt	OC not given μH not given μP 220.3(8)		μP,Pt 53.4	
(Et$_3$P)$_2$Pt(μ-H){μ-η^1;η^5-C$_2$B$_9$H$_{10}$)Ru(CO)$_2$ (yellow)	m P2$_1$/c 4	1877.4(4) 1209.4(2) 1342.9(3)	 110.78(2)	PtP$_2$HBRu	P$_{Et}$ 224.8(2) 236.9(2) μH 155.7 μB 206.9(7)	Ru 280.2(1) H 112.1(1) B 81.5(2)	P,P 108.0(1) μH,μB 88.4(2) P,μH 70.7(1) 172.7(1) P,μB 93.6(2) 157.9(2) μH,Ru 36.9(1) μB,Ru 51.6(2)	177
				RuC$_4$B$_3$HPt	OC 185.9(9,22) μηC 223.7(7,1) μηB 229.0(7,33) μB 221.9(6) μH 181.7		C,C 88.6(3) C,μH 85.9(2,1.5) μH,Pt 31.0(1)	
(η^4-cod)Pt{μ-η^2;η^4-PhCC(H)-C(H)CPh}Fe(CO)$_3$ (yellow)	m P2$_1$/c 4	1049.8(5) 1548.6(6) 1480.9(5)	 104.15(3)	PtC$_6$Fe FeC$_7$Pt	ηC 221(3,3) μC 203(2,2) OC 175(3,2) ηC 210 ημC 221(2,1)	Fe 283.0(3) C 83.8(7,1)	μC,μC 79.7(8) μC,Fe 50.9(6,3) μC,μC 71.9(7) μC,Pt 45.4(5,4)	178
[(Ph$_3$P)Pt{μ-η^1;η^5-S(Me)C$_5$H$_4$}$_2$Fe](BF$_4$)$_2$ (red)	tr_ P1 2	1294.7(3) 1296.0(7) 1159.6(2)	101.20(3) 108.94(2) 94.87(3)	PtS$_2$PFe	μηS 227.7(3,4) P$_{Ph}$ 224.9(3)	Fe 285.1(2)	S,S 164.8(1) S,P 97.5(1,1) S,Fe 83.18(9,18) P,Fe 177.12(7)	179
				FeC$_{10}$Pt	ηC 207(2,3)		C,C 91.5 -131.4(4)	
(Ph$_3$P)Pt(μ-η^1;η^5-SC$_5$H$_4$)$_2$Fe (red)	m P2$_1$/c 4	1416.6(1) 1720.8(4) 1222.7(1)	 92.52(1)	PtS$_2$PFe	μηS 229.7(4,3) P$_{Ph}$ 220.1(3)	Fe 293.5(2)	S,S 165.3(1) S,P 97.4(1,4.2) S,Fe 82.3(1,3) P,Fe 170.9(1)	180
				FeC$_{10}$Pt	μηC not given		not given	

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]Four member metallocyclic ring. [d]Three member metallocyclic ring. [e]Five member metallocyclic ring.

In three yellow derivatives a Pt-Ru bond, 274.8(1) [174], 280.2(1) [177], or a Pt-Fe bond 280.0(4) pm [173] is spanned by a hydride and μ-CHC(O)Me [174], μ-BL [177] or μ-Pcy$_2$ [173].

In the remaining two red Pt/Fe derivatives the Pt-Fe bonds of 285.1(2) [179] and 293.5(2) pm [180] are spanned by two μ-η^1:η^5-S(Me)C$_5$H$_4$ groups in the former, and by two μ-η^1:η^5-SC$_5$H$_4$ groups in the latter. The mean Pt-S bond distances are 227.7 and 229.7 pm, respectively.

The date in Table 5 indicates the shortest Pt-Fe bond to be 250.62(9) pm [150], with a range up to 293.5(2) pm [180] and a mean value of 272.4 pm. The mean Pt-X-M bridge angle opens with decreasing covalent radius of the X atom in the sequence: 57.1° (I, 133 pm) < 73.5° (P, 106 pm) < 80° (C, 77 pm).

2.2.5 Co, Rh, Ir, Ni and Pd

There are over fifty coloured PtM derivatives with these heterometals listed in Table 6. The structures are referenced in order of increasing Pt-M bond length, and are complex with several types of bridges spanning the Pt-M bonds.

In thirteen derivatives the Pt-M bonds are spanned by a pair of almost parallel μ-η^2-ligands to form two five membered bimetallic rings. These are: Pt-N-C-N-Pd [181-184], Pt-N-C-P-Pd [194], Pt-S-C-N-Rh [190], Pt-P-C-P-M (M = Pd [191], Rh [200], Ir [204]), Pt-P-C-As-Rh [202] and Pt-N-C-O-Pd [215]. The mean X-Pt-X angles deviate from the ideal 180° in the order: 176.5° (X = S) < 175.0° (N) < 171.5° (P). The mean X-M-X angles deviated from ideal in the order: 174.5° (X = N) < 171.3° (As) < 170.5° (P).

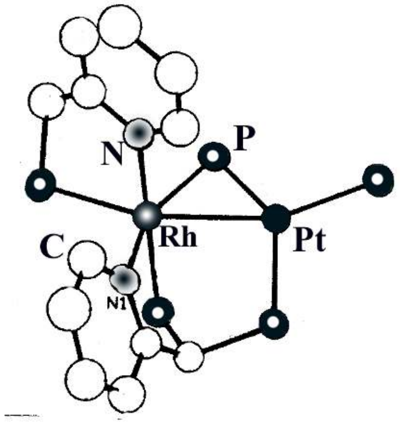

Figure 8. Structure of Structure $[(Ph_3Pt(\mu\text{-}\eta^2\text{:}\eta^1\text{-pnp})Rh(\eta^2\text{-pnp})]^{+2}$ [203]

In two PtNi [185,186] and one PtCo [185] case the Pt-M bonds (Pt-Ni, 253.7 pm (av.) and Pt-Co, 257.3(2) pm) are spanned by four 4-methyl-pyridine-2-thiolate ligands to form four five membered bimetallic rings (Pt-S-C-N-M), with all of them having a common Pt-M linkage.

The Pt-M bond in red PtNi complex (258.92(9) pm) [189] is spanned by a μ-CL ligand and a pair of μ-η^2-dppm-P,P' ligands. In a purple PtNi complex (268.9(2) pm) [201] and a yellow PtRh complex (280.1(2) pm) [210] the spanning bridges are a μ-H and a pair of μ-η^2-dppm-P,P' ligands.

There are fourteen examples in which the Pt-M bond is spanned by two single atoms: Pt-Pd (265.71(9) pm) by $(\mu\text{-}PPh_2)_2$ [194]; Pt-Rh (278.6 pm, av.) [205,206,211]; Pt-Ir (274.84(2) pm) by μ-H and μCL); Pt-Ir (268.6 pm, av.) by $(\mu\text{-}H)_2$ [197-199]; Pt-Ir (292.97(8) by μ-H and μ-BL [216]; Pt-Rh (293.4(2) and 294.5(3) pm) by μ-H and μ-SiL [217]; Pt-Co (296.7(2) pm) by a pair of μ-OH groups [219].

There are six examples in which the respective Pt and M fragments are together only by the Pt-M bond; Pt-Co (268.9 pm, av.) [192,193,196,209] and Pt-Rh (275.0(1) pm) [208].

In the yellow PtPd derivative [195] the Ph_3Pt and $PdPh_3$ fragments are spanned by a μ-Br and μ-η^2-allyl group, with Pt-Br-Pd bond angle of 63.64(4)° and Pt-Pd bond length of 267.5(1) pm.

The structure of an orange PtRh derivative [203] is shown in Fig. 8. It contains a well separated dipositive cation and two BF_4^- anions, and a methylene chloride and a diethyl ether solvate molecule in the asymmetric unit. The Pt-Rh bond of 270.8(1) pm is spanned by one pnp and one PPh_2 ligand, such that the geometry around the Pt atom is four coodinate, approximately planar (PtP_3Rh) while the geometry around the Rh atom is distorted octahedral (RhP_3N_2Pt). In the latter, the P atoms are arranged cis and occupy one trigonal face. Both pyridyl groups are part of the five membered PN chelate rings with the Rh atom, and the angles deviate from the ideal value of 90° because the ring bite angles (P5-Rh-N1, 79.4(3)°, and P4-Rh-N2, 79.4(3)°) are constrained. The most significant distortion from octahedral geometry about the Rh atom results from the symmetrically bridging PPh_2 group. The Pt-Rh-P2 angle is small (53.8(1)°) while the P2-Rh-P4 and P2-Rh-P5 angles are large at 110.4° and 102.5°, respectively. The significant distortion from square planar about the Pt atom has the same cause. The Rh-Pt-P2 angle (53.4(1)°) should be 90° and the P1-Pt-P2 angle (137.3(1)°) should be 180° As a result the P2-Pt-P3 and P1-Pt-P3 angles are forced open to 111.3(1)° and 109.5(1)°, respectively.

The structure of a purple PtRh derivative [220] consists of a well separated cation and a BF_4^- anion with a methylene chloride solvate molecule. The structure of this complex is shown in Fig. 9. The cation is bent with the dithiolate unit acting as a bridging ligand between the metal atoms, creating a doubled five membered metallocyclic ring (Pt-S-CH_2-CH_2-S/Rh-S-CH_2-CH_2-S) with mean Pt-S-Rh bridge angles of 77.9°. The Pt-Rh bond distance of 298.26(9) pm is the longest in this series.

A summary of all of the Pt-M bond distances where M is a transition is given in Table 7.

The mean Pt-X-M bridge angle opens with decreasing covalent radii of the X atom in the sequence: 63.6° (Br, 114 pm) < 72.2° (P, 106 pm) < 77.9° (S, 102 pm) < 84.6° (C, 77 pm) < 97.7° (O, 73 pm) < 105.5° (H, 37 pm). Two exceptions are where X = B (74.9° , 82 pm) and Si (77.5°, 117 pm).

There are two examples [186,188] which contain two crystallographically independent molecules differing mostly by degree of distortion. These are examples of distortion isomerism [75].

A red compound $[(H_3N)_2Pt(\mu\text{-mecyt})_2Pd(NH_3)][Pd(NH_3)_4)].5(NO_3)_3.3H_2O$ [182] contains within the same crystal a hetero binuclear (PtPd) plus a Pd monomer, and is also an example of polymerisation isomerism

2.3 Compounds with actinides

There are no examples with lanthanide metals and only one example with an actinide metal which has a Pt-M distance of less than 300 pm. The one example is a PtTh derivative, the red-brown $(Me_3P)Pt(\mu\text{-}PPh_2)_2Th(5\text{-}cp^*)_2$ [221]. The structure of this complex is shown in Fig. 10. The $(Me_3P)Pt$ fragment and the $Th(cp^*)_2$ fragment are linked by a Pt-Th bond at 298.4 (1) pm and doubly bridged by a pair of PPh_2 groups with mean Pt-P-Th bridge angel of 68.5°.

Inspection of the Pt-M (transition metal) derivatives (Tables 2-6) reveals 195 heterobinuclear platinum compounds with a Pt-M bond. The M atom includes

Table 6. Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$[(MeCH_2N)_2.Pt(\mu-\eta^2-mecyt)_2.Pd(\eta^1-meim)](NO_3)_2$ (red)	m $P2_1/c$ 4	783.0(2) 1949.5(2) 1697.2(6)	 102.12(4)	PtN_4Pd PdN_3Pt	N[b] 202(1,2) μηN 203.7(8,1) N 202.0(8) μηN 201.0(8,4)	Pd 250.97(8)	N,N[b] 174.6(3,3) N,N 173.193 N,Pt 176.8(3)	181
$[(H_3N)_2Pt(\mu-\eta^2-mecyt)_2Pd(NH_3)][Pd(NH_3)_4].0.5(NO_3)_3.3H_2O$ (red)	tr $P\bar{1}$ 2	747.6(2) 1137.3(3) 1639.7(4)	82.27(2) 85.32(2) 88.74(2)	PtN_4Pd PdN_3Pt PdN_4 (monomer)	H_3N 204.4(6,4) μηN 203.4(6,3) H_3N 204.2(7) μηN 199.7(6,1) H_3N 203.7(7,5)	Pd 251.1(1)	N,N 90.0(2,1.5) 175.6(2,1.2) N,Pd 89.4(2,3.9) N,N 92.8(3,6) 174.5(3) N,Pt 87.3(2,1) 175.7(2) N,N 90.5(3)	182
$[(H_3N)_2Pt(\mu-\eta^2-mecyt)_2.Pd(NH_3)].(NO_3)_2.3H_2O$ (red)	tr $P\bar{1}$ 2	720.7(2) 1169.2(3) 1545.7(4)	108.89(1) 101.13(1) 92.79(1)	PtN_4Pd PdN_3Pt	H_3N 203.8(5,1) μηN 201.8(4,7) H_3N 200.1(5) μηN 201.0(5,5)	Pd 251.1(1)	N,N 176.7(2,1.5) N,Pd 87.8(1,4) N,Pt 86.7(1,6) 178.5(2)	183 184
$(H_3N)_2Pt(\mu-\eta^2-mecyt)_2.Pd(\eta^1-meu)]NO_3.3H_2O$ (red-brown)	tr $P\bar{1}$ 2	995.6(5) 106.19(6) 1446.0(4)	68.66(4) 85.88(3) 67.10(4)	PtN_4Pd PdN_3Pt	H_3N 202.9(5,8) μηN 202.0(4,0) ηN 205.6(4) μηN 199.0(4,5)	Pd 251.5(4)	N,N 176.0(2,3) N,Pd 87.4(1,6) N,Pt 86.8(1,3) 178.3(2)	183 184
$[(H_3N)_2Pt(\mu-\eta^2-mecyt)_2.PdCl]NO_3.H_2O$ (olive green)	tr $P\bar{1}$ 2	911.6(4) 1050.8(6) 1137.0(6)	115.33(2) 90.00(3) 92.62(3)	PtN_4Pd PdN_2ClPt	H_3N 202.0(5,2) μηN 202.3(4,2) μηN 198.5(5,5) Cl 231.3(1)	Pd 251.8(1)	N,N 174.7(2,5) N,N 173.5(2) Cl,Pt 174.03(5)	183 184
$(MeH_2N)_2Pt(\mu-\eta^2-mecyt)_2.Pd(SCN)]NO_3.H_2O$ (green)	or $Pca2_1$ 4	1420.0(2) 1149.7(1) 1416.1(5)		PtN_4Pd PdN_2SPt	N 204.4(10,4) μηN 202.5(10,5) μηN 200.5(10,15) NCS 228.8(4)	Pd 252.1(1)	N,N 176.1(5,1.2) N,N 172.8(4) S,Pt 176.0(1)	183 184
$[Pt(\mu-\eta^2-mpyt)_4Ni(NCMe)]$ (red)	or Pbca 8	2136.2(3) 1823.7(2) 1660.8(2)		PtS_4Ni NiN_5Pt	μηS 232.2(2,2) μηN 211.9(5,11) 211.9(5)	Ni 253.1(1)	S,S 90.00(6,85) N,N 90.9(2,2.5)	185
$Pt\{\mu-\eta^2-mpyt)_4Ni(NCMe)$[c] (dark green)	or $P2_12_12_1$ 8	1660.3(1) 2134.3(1) 1822.0(1)		PtS_4Ni NiN_5Pt PtS_4Ni NiN_5Pt	μηS 224.5(10,25) 235(1,1) μηN 206(2,7) 228(2,3) N not given μηS 229.5(10,25) 239.5(10,15) μηN 202(2,4) 220(2,3) N not given	Ni 253.4(4) Ni 254.5(4)	not given not given not given not given	186
$(Ph_3P)_2Pt(\mu-CH_2)Co(\eta^5-cp)$ (orange red)	m $P2_1/c$ 4	1224.0(6) 1739.5(8) 1788.7(9)	 97.36(3)	PtP_2CCo CoC_6Pt	P_{Ph} 224.8(3) 235.6(3) μC 209.6(12) μ^5cpC not given μC 195.9(12)	Co 254.7(2) C 77.7(4)	P,P 107.9(2) P,μC 93.1(3) 159.0(3) P,Co 110.3(2) 141.4(1) μC,Co 48.7(3) μC,Pt 53.5(3)	187
$ClPt(\mu-\eta^2-Me_2Ppy)_2PdCl$[c]	m $P2_1/n$ 8	1653.2(2) 1920.5(3) 1326.0(2)	 93.86(2)	MNPClM' MNPClM'	ηN 212.7(9,5) ηP 218.9(4,1) Cl 242.0(4,4) ηN 212.9(11,11) ηP 219.0(4,8) Cl 241.9(4,9)	M 255.4(1) M' 256.8(1)	N,P 170.5(3,2) N,Cl 91.4(3,1.1) P,Cl 97.7(1,1.2) N,M 92.9(3,8) Cl,M' 173.5(1,3.6) P,M' 78.4(1,5) N,P 171.4(1,3.4) N,Cl 91.3(3,1) P,Cl 97.3(1,1.4) N,M' 93.1(3,9) Cl,M' 173.1(1,7) P,M' 78.5(1,5)	188
$[Pt(\mu-\eta^2-mpyt)_4Co(NCMe)].MeCN$ (red)	or Pbca 8	2138.1(4) 1829.2(4) 1669.2(5)		PtS_4Co CoN_5Pt	μηS 232.8(5,5) μηN 215.5(10,15) N 217(2)	Co 257.3(2)	S,S 90.0(2,1.1) N,N 91.2(6,2.3)	185
$[ClPt)\mu-CNMe)(\mu-\eta^2-dppm)_2.Ni(CNMe)]Cl.2MeCN$ (red)	m $P2_1/n$ 4	1532.4(1) 1835.4(2) 2019.0(2)	 not given	PtP_2CClNi NiC_2P_2Pt	μηP not given μC not given Cl not given	Ni 258.92(9) C not given	P,P 173.47(6) μC,Cl 163.2(2) P,P 140.65(7) C,μC 146.7(3)	189

Continued **Table 6.** Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
[(Ph$_3$P)Pt(μ-η^2-bzta)$_2$Rh(CO)Cl].CH$_2$Cl$_2$ (green)	tr $P\bar{1}$ 2	1142.5(1) 1181.9(1) 1439.3(1)	107.88(1) 99.85(1) 93.43(1)	PtS$_2$PRh	μηS 230.8(1,2) P$_{Ph}$ 224.9(1)	Rh 262.66(4)	S,S 176.39(5) S,P 90.26(5,48) S,Rh 90.19(4,54) P,Rh 165.71(4)	190
				RhN$_2$CClPt	μηN 204.3(4,3) OC 184.1(4) Cl 233.8(1)		N,N 177.9(1) C,Cl 176.6(2) C,Pt 83.7(1) Cl,Pt 99.08(4)	
ClPt(μ-η^2-dppm)$_2$Pd(C$_6$F$_5$) (deep yellow)	m P2$_1$/c 4	1628.0(4) 1295.9(4) 2503.3(10)	91.42(3)	PtP$_2$ClPd	μηP 226.9(4,2) Cl 244.4(4)	Pd 264.3(1)	P,P 178.7(1) P,Cl 89.8(1,5) P,Pd 90.3(1,1.1) Cl,Pd 178.7(1)	191
				PdP$_2$CPt	μηP 226.6(4,6) C 207.6(14)		P,P 174.0(1) P,C 93.0(4,2) P,Pt 87.0(1,8) C,Pt 175.9(4)	
(Ph$_3$P)(OC)(Ph)PtCo(CO)$_3$.(PPh$_3$)	m P2$_1$/c 4	1823.1(2) 1077.7(2) 2104.3(1)	90.338(7)	PtC$_2$PCo	OC 186(1) C$_{Ph}$ 205(1) P$_{Ph}$ 228.9(3)	Co 264.5(2)	C,C 173.3(5) C,P 93.1(4,5.1) C,Co 86.9(3,5.7) P,Co 178.6(1)	192 193
				CoC$_3$PPt	OC 177(1,1) P$_{Ph}$ 217.9(3)		C,C 113.4(5,4.4) 130.3(5) C,P 95.9(4,2.9) C,Pt 68.2; 82.2(2) 108.5(4) P,Pt 152.1(1)	
[(C$_6$F$_5$)$_2$Pt(μ-PPh$_2$)$_2$.Pd(PPh$_3$)$_3$].2C$_6$H$_6$ (dark violet)	m C2/m 4	1677.4(5) 1940.4(4) 1941.6(4)	111.54(3)	PtC$_2$P$_2$Pd	C 207.7(6,0) μP 235.4(2,0)	Pd 265.71(9) P 70.57(9,0)	C,C 84.7(4) μP,μP 105.05(9) C,μP 169.8(2,0) C,Pd 137.3(2) μP,Pd 52.75(4)	194
				PdP$_3$Pt	P$_{Ph}$ 227.2(2) μP 224.3(2)		P,μP 123.46(4) μP,μP 112.83(9) P,Pt 177.84(7) μP,Pt 56.68(4)	
(Ph$_3$P)(OC)(Me)PtCo(CO)$_3$.(PPh$_3$)	tr $P\bar{1}$ 2	1337.5(9) 1468.7(7) 1083.2(9)	108.64(5) 111.40(6) 76.40(5)	PtC$_2$PCo	PC 184.6(10) C$_{Me}$ 206.2(9) P$_{Ph}$ 226.1(2)	Co 265.8(2)	C,C 175.7(4) C,P 91.9(2,4.3) C,Co 88.1(3,5.6) 176.75(8)	193
				CoC$_3$PPt	OC 159(2) 171(1,0) P$_{Ph}$ 217.3(2)		C,C 118.0(6,6.6) C,P 79.7(3) 97.8(3,2.0) C,Pt 72.9(5,6.8) 103.5(3) P,Pt 155.28(9)	
[(Ph$_3$P)Pt(μ-Br)(μ-η^2-allyl).Pd(PPh$_3$)].CH$_2$Cl$_2$ (yellow)	tr $P\bar{1}$ 2	1353.4(2) 1414.2(3) 1167.6(3)	111.40(2) 96.71(2) 92.34(2)	MCPBrM'	μηC 205.5(10,5) P$_{Ph}$ 223.8(1,7) μBr 253.7(1,6)	M 267.5(1) Br 63.64(4)	P,M' 170.35(9,3.35)	195
(η^2-dppe)(Me)PtCo(CO)$_4$	m P2$_1$/n 4	1074.1(6) 1771.6(7) 1598.2(5)	103.56(3)	PtP$_2$CCo	not given	Co 268	not given	196
				CoC$_4$Pt	not given		not given	
[(Et$_3$P)(Et)Pt(μ-H)$_2$.Ir(H)(PEt$_3$)$_3$].BPh$_4$ (yellow)	m P2$_1$/n 4	2198.6(3) 997.0(2) 2481.1(3)	93.20(2)	PtH$_2$CPIr	μH not given C$_{Et}$ 204.4(20) P$_{Et}$ 222.4(4)	Ir 268.2(1) H not given	C,P 88.4(5) C,Ir 131.1(4) P,Ir 140.5(1)	197
				IrH$_3$P$_3$Pt	μH not given H not given P$_{Et}$ 233.0(4,10)		P,P 96.9(1,1.4) 163.8(2) P,Pt 88.1(1,1.4) 134.3(1)	
[(Et$_3$P)$_2$Pt(μ-H)$_2$Ir(H)$_2$(PEt$_3$)$_2$].BPh$_4$ (yellow)	m P2$_1$/c 4	1948.5(3) 1527.5(3) 2018.6(3)	118.78(5)	PtH$_2$P$_2$Ir	μH 160(9,7) P$_{Et}$ 227.5(3,1)	Ir 268.5(1) H 96.1(3.7) 105.5(4.0)	μH,μH 87.0(4.7) P,P 97.8(1) 87.6(3.7, 5.4) 171.6(3.1,2.4)	198
				IrH$_4$P$_2$Pt	H not given μH 188(10,18) P$_{Et}$ 229.7(2,4)		P,Ir 131.1(1,4) μH,μH 71.2(3.9) 174.94(10,71) P,P 168.9(1) P,Pt 95.6(1,8)	

Continued **Table 6.** Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
by neutron diffraction	m $P2_1/c$ 4	1898.9(10) 1531.4(3) 1979.2(6)	 118.73(3)	PtH_2P_2Ir IrH_4P_2Pt	μH 173.1(3,5) P_{Et} 227.6(2,1) H 158.9(3,3) μH 188.1(3,2) P_{Et} 230.0(2,1)	Ir 267.791) H 95.5(1,2)	μH,μH 88.70(13) P,P 96.87(6) μH,P 87.25(10,14) 174.94(10,71) P,Ir 131.56(6,28) H,H 76.99(15) μH,μH 84.42(13,4.29) P,P 168.9(6) P,Pt 95.54(2,51)	198
[(Et$_3$P)(Ph)Pt(μ-H)$_2$Ir(H)(PEt$_3$)$_3$]. BPh$_4$ (yellow)				PtH_2CPIr IrH_3P_3Pt	μH not given C_{Ph} 208(2) P_{Et} 221.3(6) H not given μH not given P_{Et} 233.9(5,16)	Ir 268.7(2)	C,Ir 133.0(3) P,P 95.6(2,1.1) 165.7(1) P,Pt 88.9(1,2.3) 138.2(1)	199
[(MeNC)Pt(μ-η^2-dppm)$_2$. Rh(CNMe)$_2$Cl](PF$_6$)$_2$. 0.5MeCN (yellow) at 130K	tr $P\bar{1}$ 2	1146.5(4) 1483.2(6) 1971.2(10)	87.71(4) 79.43(4) 67.88(3)	PtP_2CRh RhC_2P_2ClPt	μηP 230.5(2,5) MeNC 196.0(10) MeNC 196.9(9,8) μηP 233.9(4,3) Cl 251.6(3)	Rh 268.8(2)	P,P 169.0(1) P,C 90.2(2,2.5) P,Rh 91.1(1,6) C,Rh 166.4(3) C,C 170.3(4) P,P 170.7(1) C,Pt 85.5(3,4.1) P,Pt 94.7(1,6) Cl,Pt 173.1(1)	200
ClPt(μ-CO)(μ-η^2-dppm)$_2$NiCl (purple)	m $P2_1/n$ 4	1951.1(12) 1812.2(9) 1393.6(10)	 99.72(5)	PtP_2CClNi NiP_2CClPt	μηP 231.5(4,9) μOC 203(1) Cl 237.4(5) μηP 220.8(4,1) μOC 177(2) Cl 227.4(4)	Ni 268.9(2) C 89.8(6)	P,P 172.8(1) P,μC 89.6(4,2.1) P,Cl 91.6(2,3) μC,Cl 161.6(5) P,P 146.0(2) μC,Cl 149.9(5) P,μC 88.8(5,1.7) P,Cl 99.2(2,6.6)	201
[(Et$_3$P)(Ph)Pt(μ-H)$_2$Ir(H)(PEt$_3$)$_3$]. BPh$_4$	m $P2_1/a$ 4	2057.8(2) 1504.6(1) 1822.3(1)	 94.53(1)	PtH_2CPIr IrH_3P_3Pt	μH not given C_{Ph} 210.1(17) P_{Et} 222.4(6) H not given μH not given P_{Et} 234.2(5,12)	Ir 269.0(1) H not given	C,P 87.0(5) C,Ir 132.8(5) P,Ir 140.2(1) P,P 95.5(2,7) 165.9(2) P,Pt 88.9(1,1.9) 138.1(1)	197
[ClPt(μ-η^2-dapm)$_2$Rh(Cl)$_2$(CO)]. 2CH$_2$Cl$_2$	m $P2_1/c$ 4	1756.3(4) 1499.5(4) 2133.8(4)	 105.90(2)	PtP_2ClRh $RhCl_2As_2CPt$	μηP 229.0(3,11) Cl 236.8(3) Cl 244.8(3,63) μηAs 241.2(1,4) OC184.8(12)	Rh 269.2(1)	P,P 168.9(1) P,Cl 86.0(1,1.7) P,Rh 94.4(1,7) Cl,Rh 175.0(1) Cl,Cl 96.9(1) As,As 171.3(1) Cl,Pt 87.4(1) 175.5(1) As,Pt 93.9(1,9) C,Pt 78.2(3)	202
(MeNC)Pt(μ-η^2-dppm)$_2$Rh(I). (CNMe)$_2$](PF$_6$)$_2$ (yellow) at 130K	tr $P\bar{1}$ 2	1153.1(5) 1468.2(6) 1984.9(14)	86.210(5) 78.260(5) 68.77(3)	PtP_2CRh RhC_2P_2IPt	μηP 230.4(3,5) MeNC 196.3(10) MeNC 196.9(9,14) μηP 235.9(3,2) I 280.7(2)	Rh 270.3(2)	P,P 169.2(1) P,C 89.9(2,2.3) P,Rh 91.3(1,3) C,Rh 167.5(3) C,C 168.8(4) P,P 171.2(1) P,Pt 94.4(1,7) C,Pt 84.6(3,4.7) I,Pt 175.0(1)	200
[(MeNC)Pt(μ-η^2-dppm)$_2$. Rh(CNMe)$_3$](PF$_6$)$_2$. 0.46(MeCH$_2$)$_2$.0.54MeCN (yellow) at 130K	m $P2_1/n$ 4	1572.4(6) 1815.7(5) 2513(3)	 97.52(5)	PtP_2CRh RhC_3P_2Pt	μηP 231.4(4,3) MeNC 197(1) MeNC 196(2,1) μηP 233.9(4,5)	Rh 270.8(2)	P,P 177.6(1) P,C 88.9(4,1.2) P,Rh 91.2(1,2) C,Rh 175.9(4) C,C 176.7(5) P,P 172.3(1) C,Pt 91.4(4,2.2) P,Pt 86.3(1,2)	200
[(Ph$_3$P)Pt(μ-PPh$_2$)(μ-η^2:η^1-pmp). Rh(η^2-pmp)](BF$_4$)$_2$. CH$_2$Cl$_2$.Et$_2$O (orange)	m $P2_1/c$ 4	1592.1(9) 1612.8(3) 3332.6(9)	 101.44(2)	PtP_3Rh RhP_3N_2Pt	P_{Ph} 231.5(3) μP 228.7(3) μηP 232.4(3) P 233.2(3,50) μηP 227.6(3) N 216(1,4)	Rh 270.8(1) P 73.8(1)	μP,Rh 53.4(1) P,Pt 84.2(1) 163.4(1) μP,Pt 53.8(1) N,Pt 96.2(3,2.5)	203

Continued **Table 6.** Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(Me_3P)_2(Rh)PtCo(CO)_4$	or $P2_12_12_1$ 4	1289.4(3) 1412.1(2) 1157.1(2)		PtP_2CCo	P_{Me} 231.5(4,3) C_{Ph} 206(1)	Co 271.1(2)	P,P 172.8(2) P,C 90.7(4,3) P,Co 92.8(1,1.9) C,Co 164.3(5)	193
				CoC_4Pt	OC 182(2,6)		C,Pt 67.5(5,7.2) 126.3(7,5.1)	
$[Pt(\mu-\eta^1:\eta^2-dpmp)_2Ir(CO)Cl](PF_6)_2$ (yellow) at 130K	m $P2_1/c$ 4	1862.0(14) 1819.5(13) 2053.9(7)	94.03(5)	PtP_3Ir	P 225.6(5) 232.2(5,19)	Ir 273.0(2)	P,P 72.9(2)[d] 102.4(2) 174.3(2) P,Ir 91.9(1,2.0) 158.2(1)	204
				IrP_3CClPt	P 233.8(5) 239.0(6,20) OC 184(2) Cl 241.7(5)		P,Pt 92.6(1,1.6) 158.1(1) C,Pt 87.6(7) Cl,Pt 76.9(1)	
$(Et_3P)_2Pt(\mu-H)(\mu-CO).Rh(\eta^5-C_2B_9H_{11})(PPh_3)$ at 190K	tr $P\bar{1}$ 2	1038.9(6) 1150.6(5) 1874.2(5)	101.23(3) 93.78(3) 113.23(3)	PtP_2HCRh	P_{Et} 227.5(4) 235.5(4) μH 180(20) μOC 199(1)	Rh 273.4(2) H 102(9) C 86.7(5)	P,P 100.0(1) μH,P 84(6) 176(5) μC,P 95.2(4) 164.6(4) P,Rh 129.0(1,9.7) μC,Rh 46.7(4)	205
				RhC_3B_3HPPt			μH,P 85(4) P,Pt 100.8(1) μC,Pt 46.7(4) μC,P 90.7(3)	
$(I)Pt(\mu-\eta^2-dapm)_2Rh(CO)(I)_2$	or Pbca 8	1780.8(8) 1948.8(8) 3522.8(15)		PtP_2IRh	μηP 233.3(7,0) I 267.3(2)	Rh 273.7(3)	P,P 169.4(2) P,I 87.0(2,1.2) P,Rh 93.7(2,2) I,Rh 170.6(1)	202
				$RhAs_2I_2CPt$	μηAs 240.7(4,7) I 270.9(3,23) OC 184.8(12)		As,Pt 93.9(1,9) I,Pt 87.4(1) 175.5(1) C,Pt 78.2(3)	
$(Et_3P)_2Pt(\mu-H)(\mu-CO).Rh(\eta^5-C_2B_9H_{11}(PPh_3)$ (orange)	m $P2_1/n$ 4	1102.4(1) 2331.4(2) 1667.0(1)	93.856(7)	PtP_2HCRh	P_{Et} 228.2(2) 233.4(2) μH 175.7 μOC 201.4(8)	Rh 274.8(1) H 116.1(1) C 87.0(3)	P,P 102.6(1) P,μH 91.2(1) 162.5(1) P,μC 92.0(2) 165.3(2) P,Rh 119.9(1) 135.3(1) μC,Rh 46.0(2)	206
				RhC_3B_3HPPt	η^5C 233.1(7,21) ηB 224.0(9,23) μH 147.7 μOC 197.8(7) P_{Ph} 231.2(2)		μC,P 93.7(2) μH,P 95.0(1) P,Pt 100.9(1) μC,Pt 47.0(2)	
$[(Ph_3P)_2Pt(\mu-H)(\mu-\eta^1:\eta^2-CH=CH_2).Ir(CO)(PPh_3)_2].CF_3SO_3$ (bright yellow)	tr $P\bar{1}$ 2	1332.1(1) 1546.1(2) 1775.3(2)	90.37(1) 95.47(1) 100.92(1)	PtP_2HCIr	P_{Ph} 224.4(1) 232.1(1) μH 143 μC 201.4(4)	Ir 274.84(2) H 127.23(1) C 82.1(2)	P,P 101.06(4) μH,μC 68.6(1) P,μH 102.25(3) 149.21(3) P,μC 91.4(1) 166.0(1) P,Ir 115.70(3) 142.73(3)	207
				IrC_3P_2HPt	OC 186.5(5) ηC 219.7(4) μC 216.8(4) P_{Ph} 235.0(1,13) μH 164		μH,Ir 28.34(1) μC,Ir 51.4(1) μC,Pt 46.5(1) P,Pt 125.71(3,1.54) μH,Pt 24.43(0)	
$(C_6F_5)_2(OC)PtRh(CO)_2(\eta^5-cp)$	or $P2_12_12_1$ 4	763.21(10) 1641.51(17) 1652.00(43)		PtC_3Rh	OC 186.0(9) C 204.4(7,19)	Rh 275.0(1)	C,C 89.6(3,2.2) 177.0(3) C,Rh 90.7(2,3.0) 171.8(2)	208
				RhC_7Pt	OC 187.8(10,11) ηC_{cp} 225.2(7,17)		C,Pt 84.3(3,4.4) 97.7(2) 171.8(2)	
$(Ph_3P)(\eta^2-cyclenP)PtCo(CO)_4$ (yellow)	tr $P\bar{1}$ 2	1037.4(4) 1085.7(6) 1608.6(9)	78.93(4) 83.31(4) 61.93(3)	PtP_2NCo	P_{Ph} 223.4(2) ηP 224.1(3) ηN 212.3(8)	Co 275.1(2)	P,P 104.2(1) P,N 50.8(3)[e] 155.0(3) P,Co 108.0(1) 147.9(1) N,Co 97.1(3)	209
				CoC_4Pt	OC 177.9(17,12)		C,Pt 67.4(5,3) 102.8(4) 147.2(6)	

Continued **Table 6.** Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(Et_3P)\{\eta^1$-dte)Pt(μ-$\eta^2{:}\eta^5$-$C_2B_9H_{11}$). Rh(CO)(PPh_3) (tan)	tr $P\bar{1}$ 2	1195.8(3) 1410.6(3) 1659.3(3)	72.84(2) 71.08(2) 70.19(2)	PtHCBPRh	η^2H 181 μB 229.5(7) C_{dte} 203.6(4) P_{Et} 222.1(2)	Rh 276.2(1) B 74.9(2)	C,μB 150.7(3) C,P 87.8(2) μB,P 118.9(2) C,Rh 101.9(2) P,Rh 170.3(1) μB,Rh 51.8(2)	205
				RhC_3B_3PPt	OC 184.5(8) η^5C 234.1(6,2) η^5B 226.0(?) $\eta^5\mu$B 224.7(7) P_{Ph} 229.4(2)		C,P 90.1(3) C,Pt 89.5(2) P,Pt 108.4(1) μB,Pt 53.4(1)	
[(OC)Pt(μ-η^2-dppm)$_2$Ir(CO)$_2$].PF_6 (orange)	or Ccca 16	2019.24(3) 4489.1(1) 2338.86(8)		PtP_2CIr	$\mu\eta$P 231.5(2,2) OC 191.4(9)	Ir 276.74(4)	P,P 172.33(7) P,C 93.7(3,2) P,Ir 86.22(5,2) C,Ir 179.1(3)	210a
				IrC_2P_2Pt	OC 190.4(10,1) $\mu\eta$P 230.0(2,5)		C,C 120.0(4) P,P 168.92(7) C,P 119.9(2,3.2) P,Pt 84.94(5,1.06)	
[(Me)Pt(μ-CO)(μ-η^2-dppm)$_2$RhCl]. PF_6.2H_2O (yellow)	tr $P\bar{1}$ 2	1060.30(8) 1500.5(1) 1870.5(2)	68.934(5) 83.312(5) 69.529(5)	PtC_2P_2Rh	C_{Me} 207(2) μOC 232(2) $\mu\eta$P 230.1(5,3)	Rh 280.1(2) C 82.7(7)	C,μC 146.7(8) P,P 174.0(2) C,P 92.9(5,1) μC,P 87.1(5,4) C,Rh 171.3(6) μC,Rh 42.0(5)	210b
				RhP_2CClPt	$\mu\eta$P 232.7(5,11) μOC 189(2) Cl 233.5(5)		P,P 173.0(2) μC,Cl 161.0(6) Cl,Pt 143.69(14) μC,Pt 55.3(6)	
[(Ph_3P)$_2$Pt(μ-C≡CPh)(μH). Rh(PMe_3)(η^5-cp*)] (CF_3SO_3)$_2$ (yellow)	or $P2_1/n$ 4	1445.5(4) 1857.5(3) 2262.6(4)		PtP_2HCRh	P_{Ph} 230.8(3,2) μH not given μC 199(1)	Rh 282.65(8) H not given C 85.3(4)	P,P 100.4(1) P,μC 88.4(3) 171.2(3) P,Rh 129.55(7,8.3) μC,Rh 50.2(3)	211
				RhC_6HPPt	ηcp*C not given μC 218(1) P_{Me} 232.0(3)		μC,P 91.4(3,3.0) μC,Pt 44.6(3) P,Pt 93.22(8)	
[(Ph_3P)$_2$Pt(μ-H)(μ-$\eta^1{:}\eta^2$-CH=CH_2). Ir(PMe_3)(η^5-cp*)](CF_3SO_3)$_2$	m $P2_1/n$ 4	1405.3(2) 2072.5(8) 2050.9(5)	 103.80(1) 	PtP_2HCIr	P_{Ph} 227.2(3) 233.5(3) μH not given μC 201(1)	Ir 283.62(6) H not given C 85.8(5)	P,P 103.0(2) P,μC 88.9(4) 166.4(4) P,Ir 128.45(8,8.83) μC,Ir 49.1(3)	211
				IrC_7HPPt	C 224(1) μC 215(1) P_{Me} 231.8(4) ηC_{cp} not given		C,μC 36.6(5)[e] C,Pt 72.3(4) μC,Pt 45.1(3) P,Pt 94.6(1)	
[(bmik)$Pt_{0.6}$(μ-η^2-pyridonate). $Pd_{1.4}$(bmik)](NO_3)$_2$.4H_2O	tr $P\bar{1}$ 2	1243.0(2) 1264.8(3) 1290.7(4)	89.64(2) 74.57(2) 68.65(2)	MO_2N_2M'	O 201.2(9,1) N 198(1,0)	M' 285.9(1)	O,O 90.9(3) N,N 90.8(4) O,N 89.0(4,6) 175.7(3,5)	212
				PdN_4M'	N 201(1,1)		N,N 90.0(4,3.9) 178.1(5,8)	
(PPh_3Me)[(C_6F_5)$_2$Pt(μ-C=CPh)$_2$. Rh(η^4-cod)] (orange) at 200K	or $Pna2_1$?	2192.1(4) 1076.5(2) 1976.5(4)		PtC_4Rh	C 211(3,3) μC 203(3,1)	Rh 288.9(3) C not given	C,C 91.9(11) μC,μC 80.6(10) C,μC 93.9(11,7)	213
				RhC_6Pt	η^4C 213(3,1) μC 229(2,0)		C,C 90.25(2,7.0)	
[(Et)Pt(μ-H)(μ-η^2-dppm)$_2$. Pd(Me)].PF_6 (light orange)	tr $P\bar{1}$ 1	1085.3(2) 1208.0(2) 1217.9(2)	84.57(1) 72.84(1) 87.99(1)	PtP_2HCPd	$\mu\eta$P 228.8(2,12) μH not given C_{Et} 202(2)	Pd 290.88(10) H not given	P,P 175.95(9) P,C 88.0(5,2.5) C,Pd 164.8(6)	214
				PdP_2HCPt	$\mu\eta$P not given μH not given C_{Me} 220(3)		C,P 88.2(5,7) C,Pt 167.1(12)	
[(H_3N)$_2$Pt(μ-η^2-meu)$_2$. Pd(η^2-en)](NO_3)$_2$.6H_2O (orange-brown) at 233K	tr $P\bar{1}$ 2	1169.8(2) 1179.6(2) 1296.5(2)	114.94(1) 100.29(1) 111.69(1)	PtN_4Pd	H_3N 203.8(5,3) $\mu\eta$N 204.2(5,2)	Pd 292.7(1)	N,N 90.0(2,6)	215
				PdO_2N_2Pt	$\mu\eta$O 204.3(4,4) μN_{en} 202.2(6,7)		O,O 91.2(2) N,N 84.0(2)[f] O,N 92.2(2,8)	

Continued **Table 6.** Heterobinuclear Platinum Compounds with a Pt-M Bond (M = Co, Rh, Ir, Ni, Pd or Th)[a]

COMPOUND (colour)	Crys.cl. Sp.Gr. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromophore	M - L [pm]	M - M [pm] M – L - M [°]	L – M - L [°]	Ref.
$(PhMe_2P)(Cl)Pt(\mu\text{-}H).(\mu\text{-}\eta^2{:}\eta^3\text{-}B_5H_7)Ir(CO)(PPh_3)_2$ **(yellow)**	m $P2_1/n$ 4	1543.4(2) 1859.7(1) 1720.0(1)	 92.73(1)	$PtB_2HClPIr$ IrB_3P_2HCPt	μηB 221(2) μημB 213(2) μH 194(12) Cl 240.6(4) P 224.6(3) μ 226(2,3) P 241.3(3,4) μH 168(12) OC 185.4(14)	Ir 292.97(8) H not given B not given	B,μB 47.0(7)[e] B,Ir 78.2(4) μB,Ir 50.2(4) μH,Ir 33(4) Cl,Ir 110.71(10) P,Ir 157.71(10) B,Pt 77.5(4,4.7) μB,Pt 46.2(4) P,Pt 101.8(1,9.2) H,Pt 39(4) C,Pt 154.4(4)	216
$(Me_3P)\{4\text{-}FC_6H_4)_2(H)Si\}.Pt(\mu\text{-}H)\{\mu\text{-}Si(H)(C_6H_4F\text{-}4)_2.Rh(PMe_3)_3$	tr $P\bar{1}$ 2	1209.7(3) 1970.5(7) 1100.2(2)	98.25(2) 109.71(1) 79.04(2)	$PtSi_2HPRh$ RhP_3H_2SiPt	Si 231.9(5) μSi 232.3(4) μH 166 P_{Me} 229.5(5) P_{Me} 226.3(5) 235.8(5,10) H 163 μH 224 μS 236.8(4)	Rh 293.4(2) H not given Si 77.1(1)	Si,μSi 83.1(2) μH,P 73.0 Si,μH 169.4 μSi,μH 101.3 Si,P 102.7(2) μSi,P 174.1(2) P,P 98.5(2,5) H,μH 87.9 H,Si 66.66 μH,μSi 84.9	217
$[(Me_3P)\{4\text{-}FC_6H_4)_2(Cl)Si\}.Pt(\mu\text{-}H)\{\mu\text{-}Si(H)C_6H_4F\text{-}4\}.Rh(PMe_3)_3].thf$	tr $P\bar{1}$ 2	1218.9(5) 1854.7(8) 1153.6(4)	90.72(4) 104.31(3) 94.63(4)	$PtSi_2HPRh$ RhP_3H_2SiPt	Si 228.9(8) μSi 232.4(8) μH not given P_{Me} 229.8(9) P_{Me} 225.5(8) 235.8(8,12) H not given μH not given μSi 237.8(8)	Rh 294.5(3) H not given Si 77.6(2)	Si,μSi 92.6(3) Si,P 95.7(3) μSi,P 169.6(3) P,P 98.6(3,9) P,μSi 97.9(3,2.4) 153.7(3)	217
$[(\eta^1\text{-}p\text{-}MeC_6H_4C{+}C).Pt(\mu\text{-}\eta^2\text{-}dppm)_2(\mu\text{-}H).Ir(CO)(\eta^2\text{-}tb)].BF_4.2CH_2Cl_2$ **(brown)**	m $P2_1/n$ 4	1077.2(1) 2574.9(3) 2532.9(3)	 94.94(1)	PtP_2HClr IrC_3P_2HPt	μηP 229.3(5,5) C 198.5(14) OC not given ηC 209.7(13,8) μηP 235.6(5,1)	Ir 294.8(1) H not given	P,P 165.5(1) C,C 79.0(5)[f] 100.3(5) 178.7(4) P,P 169.3(1)	218
$[Cl_2Pt(\mu\text{-}OH)_2Co(\eta^2\text{-}en)_2].[PtCl_4]$ **(brown-red)**	m $P2_1/n$ 2	1260.3(5) 1456.0(3) 762.0(1)	 94.45(6)	PtO_2Cl_2Co CoN_4O_2Pt	μHO 202.4(8,4) Cl 228.5(3,3) ηN 194(1,1) μO 191.8(8,2)	Co 296.7(2) O 97.7(3,2)	O,O 78.6(3) Cl,Cl 91.0(1) O,Cl 95.2(2,7) N,N 87.2(4,3)[f] O,O 83.8(3)	219
$[(Ph_3P)_2Pt\{\mu\text{-}S(CH_2)_2\}.Rh(CO)_2].BF_4.0.5CH_2Cl_2$ **(purple)**	m $P2_1/c$ 4	1840.7 1416.2 3269.3	 100.56	PtS_2P_2Rh RhC_2S_2Pt	μS 237.3(3,4) P_{Ph} 228.9(2,8) OC 187(2,2) μS 237.0(3,0)	Rh 298.26(9) S 77.93(9,9)	S,S 78.39(10) P,P 101.34(9) S,P 90.2(1,2.3) 168.2(1,2.2) μS,Rh 50.99(7,2) C,C 90.9(7) S,S 78.51(10) μS,Pt 51.09(7,10)	220
$(Me_3P)Pt(\mu\text{-}PPh_2)_2Th(\eta^5\text{-}cp^*)_2$ **(red-brown)**	m $P2_1/n$ 4	1639.4(3) 1326.9(5) 2431.9(4)	 105.41(1)	PtP_3Th $ThC_{10}P_2Pt$	P_{Ph} not given μP not given ηcp*C not given μP 292.2(6,31)	Th 298.4(1) P 68.5(2,7)	not given μP,μP 92.0(2)	221

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]Two crystallographically independent molecules present. [d]Four membered metallocyclic ring. [e]Three membered metallocyclic ring [f]Five membered metallocyclic ring

Cu(x6), Ag(x10), Au(x5), Ti(x3), V(x1), Ta(x2), Cr(x6), Mo(x8), W(x34), Fe(x41), Ru(x7), Co(x7), Rh(x17), Ir(x10), Ni(x4) and Pd(x15). In addition there is one example for the actinides, thorium.

The coordination environments around the platinum atoms (Pt(0), Pt(II) and Pt(IV)) are square planar, trigonal bipyramidal and pseudo-octahedral (Pt(IV)), of which the first two are most common, The most important is square planar with differing degrees of distortion. There are uni-, bi-, tri-, tetra-, penta- and hexadentate ligands. The most common donor atoms are P and C. The mean Pt-P bond lengths increase in the sequences: 226.2 pm (PMe_3) < 226.3 pm (PMe_2Ph) < 226.6 pm (PEt_3) < 226.8 pm (PPh_3); for Pt-P trans to C: 231.8 pm (PMe_3) < 232.4 pm (PEt_3) < 232.6 pm (PPh_3); for Pt-P trans to H: 234.1 pm (PPh_3) < 235.5 ($PtPPh_3$). The first two sequences follow the steric effects of the respective ligands.

The mean Pt-C distances increase in the orders: 187.5 pm (CO) < 196.5 pm (CNL); 201 pm (uni-, including CO, CNL and CL) < 206 pm (bi-) < 219 pm (tri-) < 226 pm (tetradentate). The mean Pt-L bond distance for unidentate atoms or ligands increases with the covalent

Table 7. Summary of the Pt-M bond distances in Hetero-binuclear Platinum Compounds (M = transition metal and thorium)

Pt - M	Range [ref], pm	No. of examples	Average, pm
-Cr	249.50(2) [91] – 290.50(2) [128]	6	264.6
-Cu	250.10(2) [77] – 276.50(3) [83]	6	258.3
-Fe	250.62(9) [133] – 293.50(2) [180]	41	265.6
-Pd	250.97(8) [181] – 292.70(1) [215]	15	263.7
-Ni	253.10(1) [185] – 268.90(2) [201]	4	257.8
-Co	254.70(2) [187] – 296.70(2) [219]	7	269.3
-W	260.30(1) [92] – 294 [131]	34	278.6
-Mn	260.30(1) [133] – 272.80(6) [139]	8	265.3
-V	260.40(7) [91]	1	260.4
-Au	261.12(7) [40] – 300.00(1) [90]	5	278.6
-Rh	262.66(4) [190] – 298.26(9) [220]	17	277.8
-Ag	263.70(1) [79] – 24.5(1) [89]	10	274.8
-Re	264.30(1) [136] – 289.88(5) [149]	15	280.4
-Ru	266.40(1) [167] – 280.20(1) [177]	7	272.4
-Ir	268.20(1) [197] – 294.80(1) [218]	10	276.1
-Mo	276.60(1) [103] – 293.30(1) [113]	8	285.3
-Ti	278.90(3) [108] – 296.20(2) [106]	3	286.0
-Ta	Data not available [132]	2	
-Th	298.40(1) [221]	1	

radius of the donor atom, except N, Cl and Si, in the order: 158 pm (H, 37 pm) < 201 pm (CL, 77 pm) < 205 pm (NL, 75 pm) < 229.0 pm (PL, 106 pm) < 232.0 pm (SiL, 117 pm) < 234.6 pm (SL, 102 pm) < 236.0 pm (Cl, 99 pm) < 260.7 pm (Br, 114 pm) < 266.0 pm (I, 133 pm).

For homo-bidentate (non-chelating to Pt) ligands, the mean Pt-L distance increases in the order: 203 pm (NL) < 205 pm (CL) < 226.3 pm (PL) < 233.2 pm (PI, trans to C) < 238.7 pm (SL). For homo-bidentate (chelating to Pt) ligands, the order is 206 pm (CL) < 222 pm (OL) < 224.8 pm (PL) < 233.2 pm (PL, trans to C).

In the series of hetero-bidentate ligands there are two types, one donor not chelating to the Pt atom, for example O + N (av. Pt-N 204 pm); O + Si (Pt-O, 213 pm); N + S (av. Pt-S, 232.0 pm), and P + As (av. Pt-P, 229.2 pm). The other type both donors are chelating to the Pt atom, for example O + P (Pt-O, 211 pm; Pt-P, 224 pm); N + P (av. Pt-N, 212.5 pm; Pt-P, 221.5 pm); P + C (Pt-C, 206 pm; Pt-P, 224.0 pm).

The mean Pt-L(bridge) bond distances increase in the order: 185 pm (H) < 197.5 pm (CNL) < 202.4 pm (OH) < 206 pm (CL) < 218 pm (CO) < 220.5 pm (BL) < 224.5 (SL) < 232.5 pm (SiL) < 233.7 pm (Cl) < 241 pm (CH_3) < 253.7 pm (Br) < 266.3 pm (I).

In the examples with chelating ligands electronic and steric factors play a role in the resulting geometry and are reflected in the variation of the L-Pt-L ring angles of the respective metallocyclic rings. The mean L-Pt-L angle in the three membered rings opens in the order: 37.0° (CC) < 47.7° (BB) < 50.8° (NP), reflecting the radius of the donor atom. In the four membered metallocyclic rings the angle opens in the order: 73.7° (PCP) < 74.0° (SCS), and in the five membered rings the order is 73.0°(PC_2P < 84.4° (OC_2P) < 85.0° (CC_2P).

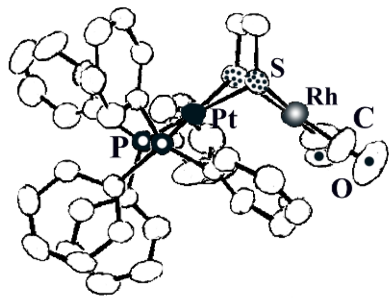

Figure 9. Structure of $[(Ph_3P)Pt(\mu\text{-}S(CH_2)_2S\}Rh(CO)_2]^{+2}$ [220]

The Pt-X-M bridge angle opens as the covalent radius of X decreases, except for B and Si atoms, in the order: 57.8° (I, 133 pm) < 63.6° (Br, 114 pm) < 70.9° (Cl, 99 pm) < 73.6° (P, 106 pm) < 76.2° (S, 102 pm) < 77.4° (B, 82 pm) < 77.5° (Si, 117 pm) < 81.7° (C, 77 pm) , 97.7° (O, 73 pm) < 106.5°(H, 37 pm).

A summary of the Pt-M bond distances (M = transition metal and Th) are summarized in Table 7. These metals allow a variety of structural forms and stabilize the metal-metal bonds. The shortest Pt-M bond distance is Pt-Cr at 249.5(2) pm [91]. The most frequently occurring transition metals are iron (41 examples) and tungsten (34 examples).

The transition metals show a wide variety of stereochemistry with the following coordination numbers: two, Ag [83,84] and Au [40, 78, 88-90]; three, Ag [81, 82, 85-87]; four, Cu [77] and Pd [181-184, 188, 191-195, 212]; five, Cu [77,83], W [124,131], Co [193, 196, 209], Rh [190, 210, 220], Ni [189, 201] and Pd [193-214]; six,

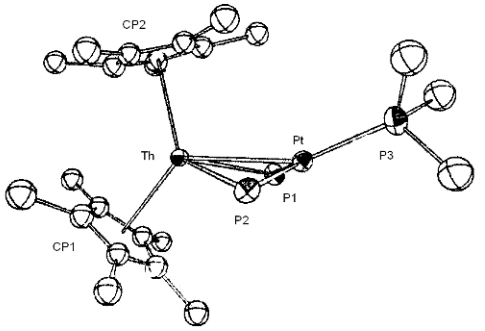

Figure 10. Structure of $(Me_3P)Pt(\mu\text{-}PPh_2)_2Th(\eta^5\text{-}cp^*)_2$ [221]

Cu [40], V [91], Cr [91,128], Mo [130], W [100,113], Mn [133], Re [143,145,148,149], Fe, [150-163,165,166,169-171,173,175], Co [185], Rh [200,202,203], Ir [204,218] and Ni [185,186]; seven, Cr [94,117], Mo [113,122], W [102,102,105,107,115,118,123], Re [136], Fe [157,164], Co [187], Rh [214,27] and Ir [197-199,207]; eight, W [125], Re [138], Fe [172,178], Rh [205,208] and Ir [216]; nine, mostly hemi-sandwiches, Mo [120,129], W [93,96,98,99,101,109,112,121,127, Mn [94,134,135], Re [140-142,144,146,147], Ru [167,168,177] and Rh [205,206,211]; ten and higher, sandwiches, Ta [132],Ti [106,119], Mo [111,114], W [93,96,97,104,106,108,116,126], Fe [179,180] and Ir [211]. In the case of thorium, the atom is sandwiched between two inclined η^5-pentamethylcyclopentadienyls, with two P atoms of the $\mu\text{-}PPh_2$ group and the Th-Pt bond (298.4(1) pm) [221].

3. Conclusions

Almost two hundred and ninety heterobinuclear Pt derivatives are reported here. Where M is a non-transition metal the binuclear are found both with and without a metal-metal bond. Where M is a transition or actinide metal only those with a metal-metal bond have been included here.

The heterometal atoms include thirteen non-transition metals: Sn (30) > Hg (18) > Ge (14) > Sb (6) > Tl (5), Zn (5) > Pb (3) > Cd (2) > Na, K, Ga, and In (1 each). There are also eighteen transition metals involved: Fe (41), W (34), Rh (17), Re and Pd (16 each), Ag and Ir (10 each), Mo and Mn (8 each), Ru and Co (7 each), Cu and Cr (6 each, Au (5), Ni (4), Ti (3), Ta (2) and V(1). Also there is one example of an actinide, thorium.

The Pt atom has oxidation number of 0, +2 and +4. The Pt coordination geometries include square planar, trigonal bipyramidal, pseudo-octahedral (Pt(IV)) and a few prevalently capped trigonal prismatic seven coordinate species. The first two geometries are the most common, with varying degrees of distorted square planar being most important.

There are four types of crystal class, monoclinic (57.4% with $P2_1/n$ predominating), triclinic (29.4%, $P\bar{1}$), orthorhombic (12.6%) and tetragonal (0.6%).

The complex $(Me_3P)_2Pt(\mu\text{-}ocp)Mn(CO)_4$ exists in two isomeric forms, yellow triclinic and red monoclinic [137], differing mostly by degree of distortion. There are several examples [26,35,50,63,91,97,137,186,188] which contain two crystallographically independent molecules, differing by degree of distortion, in the same crystal. These are all examples of distortion isomerism [76].

There are three examples [26,39,182] which contain within the same crystal a heterobinuclear and a monomer, and another with a heterobinuclear and a homobinuclear [64] and are examples of polymerisation isomerism.

The shortest Pt-M bond distances are: Pt-Ge 235.2(1) pm [7] for the non-transition derivatives; Pt-Cr 249.5(2) pm [91] for transition derivatives. The only actinide derivative has a Pt-Th distance of 298.4(1) pm [221].

It is hoped that this overview will serve to focus attention on areas of Pt chemistry that could be enhanced by further study, and assist in comparing the behaviour of the Pt atom in a variety of chemical environments. A review of the Pt-M(transition metal) derivatives without a metal metal bond is currently in progress.

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Abbreviations

ac	acetate
ad	3,7-di-tert-butyl-5-aza-2,7dioxabicyclo[3,3,0]octa 2,4,6-triene
bao	$PhC(NH_2)=NOH$
bmik	bis(N-methylimidazol-2-yl) ketone
Bu	butyl
Bu^t	ter-butyl4,
4-Bu_2bpy	4,4'-tert-butyl-2,2'-bipyridine
Bz	benzyl
C_6Cl_5	pentachlorophenyl
C_6F_5	pentafluorophenyl
C_4H_7	methylallyl
C_5H_4SMe	cyclopentadienthiomethyl
C_6H_6	benzene
C_6H_{12}	cyclohexan
C_7H_7	cycloheptatrienyl
$C_6H_{11}NC$	cyclohexylisocyanide
$C(H)(NEt_2)$	diethylaminomethylidene
Clan	p-chloroaniline
C_4Me_4	tetramethylcyclobutadiene
coc	cyclooctenyl
cod	cycloocta-1,5-diene
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
damp	2-(dimethylaminomethyl)phenyl
dapm	$Ph_2AsCH_2PPh_2$
dbpe	bis(1,2-di-tert-butylphosphino)ethane
dcpe	$Cy_2PCH_2CH_2PCy_2$
dmec	1,5-dimethylcytosine(-1)
dmpm	bis(dimethylphosphino)methane
dpb	1,3-diisopropyl-benzo-1,3,2-diazaborolidine
dpmp	bis((diphenylphosphino)methyl)phenylphosphine
dppa	(1,2-diphenylphosphino)amine
dppc	bis(1,2-diphenylphosphino)cyclopentane-1,2-diyl
dppe	bis(1,2-diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppot	$Ph_2PCH=C(O)$(p-tolyl)
dppp	bis(1,2-diphenylphosphino)propane
dppv	bis(diphenylphosphino)vinyl
dte	$C(C_6H_4Me\text{-}4)=C(C_6H_4Me\text{-}4)H$
dub	7',11'-heptahydro-7,8'-dimethyl-10'-p-tolylmethyl-7',8'-dicarbo-nido-undecaborate(-3)
en	ethylenediamine
Et	ethyl
Etgh	9-ethylguanine
hx	hexagonal
inst	$CNCH_2SO_2$-p-tolyl
ligHCl	lignocaine hydrochloride
m	monoclinic
mbo	2-mercaptobenzoxazoyl
Me	methyl
Me_2ann	8-dimethylamino-1-naphthyl

1-mec	1-methylcytosine(-1)
4-MeC_6H_4C	4-tolylmethylene
4-$MeC_6H_4N_2$	4-tolyldiazenide
mecyt	1-methylcytosinate
meim	1-methylimidazole
Me_2mal	dimethylmaleate
Me_2NCS_2	dimethyldithiocarbamate
4-MeOPhC	4-methoxy(phenyl)carbene
Me_2phen	2,9-dimethyl-1,10-phenanthroline
meu	1-methyluracilate
mppm	o-$MeC_6H_4PC_6H_4CH_2$
mpt	CH_2-C_6H_4-P(o-yolyl)$_2$
4-mpyt	4-methylpyridine-2-thiol
mtub	$C_6B_9H_8(CH_2C_6H_4Me$-4)
nbn	norbornyl(C_7H_{11})
npe	CH_2CMe_3
ocp	2-oxacyclopentylidene
or	orthorhombic
Pcy_3	tricyclohexylphosphine
PEt_3	triethylphosphine
Ph	phenyl
Ph_2Ppy	2-(diphenylphosphino)pyridine
Ph_2PthqH	hydroquinon-2-ylmethyl-diphenylphosphine
PMe_3	trimethylphosphine
PMe_2Ph	dimethylphenylphosphine
pnp	2-{bis(diphenylphosphino)methyl}pyridine
pp3	tris(2-diphenylphosphophenyl)phosphane
PPh_3	triphenylphosphine
PPh_2Me	methyldiphenylphosphine
pz_3BH	tris(pyrazol-1-yl)borate
$Si(OMe_3)_3$	trimethoxylsilyl
$SiPh_3$	triphenylsilyl
tb	C=C(C_6H_3Me)CH_2CH=$CHCH_2$
tcap	(p-tolyl)NC(H)NPr^i
thf	tetrahydrofuran
tht	tetrahydrothiophene
tg	tetragonal
tms	$N(SiMe_3)_2$
tol	toluene
tpm	p-tolyl(trimethylphosphonio)methanide
tsap	4-$MeC_6H_4S(O)_2$NHC(O)CH=C=C(Ph)
tsc	C=C(Ph)N$(S(O)_2$tolyl-p)C(O)CH_2)
tr	triclinic
ttnc	4-$MeC_6H_4S(O)_2CH_2NC$

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