Cent. Eur. J. Chem. • 11(6) • 2013 • 827-900
DOI: 10.2478/s11532-013-0226-3

VERSITA

Central European Journal of **Chemistry**

Crystalographic and structural characterization of heterometallic platinum compounds. Part III: heterotrinuclear compounds

Review Article

Milan Melník[1*], Peter Mikuš[1], Clive E. Holloway[2]

[1]*Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, SK-832 32 Bratislava, Slovak Republic*

[2]*Department of Chemistry, York University, North York, M3J 1P3. Ontario, Canada*

Received 10 October 2012; Accepted 13 January 2013

Abstract: This review article includes over three hundred and sixty heterotrinuclear platinum complexes of the composition Pt_2M (205 examples), PtM_2 (132 examples) and PtMM (24 examples). The heterometals include the non-transition and transition metals. Three metal atoms form a wide variability of frameworks: M_3 triangular, dicapped M_3 triangular, V shaped M_3, M_3 linear, five-, six- and seven- metallocycles and unique structures of which triangular and linear are the most common. This has led to a rich chemistry of platinum not only from variability of metals, but also from their framework and stereochemistry. The shortest Pt-M (non-transition) and Pt-M (transition) bonds are 2.315(1) Å for Pt-Ga and 2.4896(9) Å for Pt-Co. The shortest Pt-Pt bond distance is 2.581(1) Å. Two complexes exist in two isomeric forms and several others contain crystallographically independent molecules. All are typical examples of distortion isomerism. Correlations between structural parameters, heterometal and ligand donor atoms are developed and discussed.

Keywords: *Classification • Analyze • Structure • Heterotrinuclear • Platinum • Complexes*

1. Introduction

Heteronuclear platinum complexes containing metal-metal as well as non metal-metal bonds have been of significant interest because they serve as plausible models for the surface of heterogenerous catalysts and their reactions may mimic those on such surfaces. In homogeneous catalytic reactions, coordinative unsaturated species play an important role as intermediates, and most of these are thought to be mononuclear. X-ray data are available for more than 2,500 platinum complexes, as classified and analyzed by us [1-6]. Moreover, there are more than one thousand organometallic platinum complexes for which X-ray data are available, and which were summarized and analyzed as well [7,8].

Recently, we classified and analyzed over five hundred heterobinuclear platinum compounds [9,10]. The present review deals with the heterotrinuclear platinum compounds. There are three types: Pt_2M, PtM_2 and PtMM'. Structures are listed in the order of Pt_2M, PtM_2 and PtMM' and sorted by subgroups of M. The primary source of information has been the Cambridge Crystallographic Data Base up to the end of 2002.

2. Pt_2M compounds

2.1. Pt_2M, M is non-transition metal

Crystallographic and structural data for heterotrinuclear Pt_2M (M = non-transition metal) are gathered in Table 1. There are forty two Pt_2M derivatives which are listed in order of the elongated Pt-M bond distance.

* *E-mail: qmelnik@stuba.sk*

Two yellow $Pt(IV)_2Sn(II)$ derivatives [11] are the only examples which contain Pt(IV) atoms. Two "satellites" $(\eta^2\text{-}Bu^t_2bpy)(Me)_2ClPt$ are connected to $SnCl_2$ with a mean Pt-Sn bond distance of 2.5418 Å and a Pt-Sn-Pt angle of 136.34(2)º in one, and two $(\eta^2\text{-}Bu^t_2bpy)(Me)Cl_2Pt$ units to the Sn(Ph)Cl group with a mean Pt-Sn bond distance of 2.5720 Å and a Pt-Sn-Pt angle of 128.04(2)º in another one. In four orange-yellow $Pt(II)_2Hg(0)$ derivatives [12,13,14], pairs of $(\eta^2\text{-}Me_2phen)(\eta^2mal)(H_2O)Pt$ [12] $(\eta^2\text{-}dppen)(xylNC)Pt$, $(\eta^2\text{-}dppp)(xylNC)Pt$ and $(\eta^2\text{-}dtbpe)(xylNC)Pt$ [13,14] are held together by a single Hg(0) atom with mean Pt-Hg-Pt angles of 172º (range 163.69(5) - 180º) and a mean Pt(II)-Hg(0) bond distance of 2.610 Å (range 2.5444(5) – 2.645(2) Å).

There are three orange $Pt(I)_2Hg(II)$ derivatives [15,17,19] which contain a Pt-Hg-Pt triangle with mean Pt-Pt-Hg angles of 59.2º which are about 1.5º smaller than those of Pt-Hg-Pt, 61.7º. The mean Pt-Hg bond distances of 2.695 Å are about 0.090 Å shorter than those of Pt-Pt distances, 2.785 Å (ave.).

The dark blue $Pt(II)_2Tl(II)$ derivative [16] is the only example which contains a Tl atom in an oxidation state of +2. The structure contains well separated $[\{(C_6F_5)_4Pt\}_2Tl]^{2-}$ anions and $(NBu_4)^+$ cations. In the complex cation, a pair of $(C_6F_5)_4Pt$ satellites are held by a single Tl(II) atom, with a mean Pt-Tl bond distance of 2.703 Å and a linear Pt-Tl-Pt angle, 179(I)º.

There are two yellow $Pt(II)_2Pb(II)$ derivatives [18], in which a pair of $(C_6F_5)_3Pt$ units are bridged by μ-Pb and μ-OH or μ-Cl and form the central four-membered trimetallocycle (PtXPtPd (X=O or Cl) with Pt-Pb bond distances of 2.706 Å (mean) and 2.725 Å (mean), respectively. The Pt-Pb-Pt bridge angles are 80.5(I) and 85.25(3)º, respectively. The Pt-X-Pt bridges are 110.4(4)º (X=O) and 99.03(9)º (X=Cl). In another yellow $Pt(II)_2Hg(II)$ derivative [20], two $(C_6F_5)_3Pt$ fragments are connected by a μ-OH group with a Pt-O-Pt bridge angle of 16.0(5)º and by a $\mu\text{-}Hg(C_6F_5)$ unit with a Pt-Hg-Pt bridge angle of 80.7(I)º. The symmetrical Pt-Hg bond distances are equal of 2.718(1) Å. In another two brown $Pt(0)_2Pb(II)$ [21,22] and two red $Pt(0)_2Tl(I)$ [23] derivatives, pairs of the respective Pt(0) fragments are connected by a single Pb(II) and a single Tl(I) atom, respectively. The mean Pt-Pb-Pt and Pt-Tl-Pt angles are 178.3º and 176.9º with mean Pt-Pb and Pt-Tl bond distances of 2.760 and 2.793 Å, respectively.

The structure of the yellow $Pt(II)_2Tl(I)$ derivative [24] consists of a well separated $[\{Me_2(\mu\text{-}\eta^2\text{-}dppy)Pt\}_2Tl]^+$ cation, a ClO_4^- anion and tetrahydrofurane molecules. The structure of the complex cation is shown in Fig. 1. The 2,6-bis(diphenylphosphino)pyridine ligands adopt coordination mode D. The pair of cis-coordinated phosphorus atoms belonging to different dppy ligands are coplanar with the methyl groups and the platinum(II) atom. The Pt-Tl bond distances are 2.7961(7) and 2.8090(1) Å and the Pt-Tl-Pt angle is 157.88(2)º.

The most common type is that which contains a $Pt_2(\mu_3\text{-}X)_2M$ central core as an X-bicapped MPt_2 triangle with negligible metal-metal interactions. There are twenty two such examples in which each platinum atom is Pt(II) with a square planar geometry PtX_2P_2, where P are only PPh_3 molecules. Heterometals are found in wide varieties. In yellow $Pt_2(\mu_3\text{-}O)_2Li(I)$, an oxide-bicapped $LiPt_2$ triangle has a Pt-Pt distance of 2.969(1) Å and a Pt-O-Pt bridge angle of 94.1(3)º, which is more open than the mean Pt-O-Li angle of 80.3º [25]. Sixteen derivatives have a sulfide-bicapped MPt_2 triangle $(Pt_2(\mu_3\text{-}S)_2M$, where M=Ga(III) or In(III) [26], Tl(I) [27], Sn(IV) [28], Pb(II) [29], Bi(III) [30], Zn(II) and Cd(II) [31,32] and Hg(II) [28,32]). Another five derivatives have a selenide-bicapped MPt_2 triangle $(Pt_2(\mu_3\text{-}Se)_2M$, where M=Sn(IV [33], Pb(II) and Cd(II) [34]). The mean $Pt\text{-}\mu_3X$ bond distances elongated with a covalent radius of X are, in order: 2.028 Å (X=O, 0.73 Å) < 2.366 Å (S, 1.02 Å) < 2.478 Å (Se, 1.16 Å). The mean Pt-X-M angles open with an increasing covalent radius of X in the order: 80.3º (X=O) < 83.5º (S) < 84º (Se). On the other hand, the mean Pt-X-Pt angle closes in the same order: 94.1º (O) > 87.5º (S) > 87.3º (Se).

The structure of the $Pt(II)_2Zn(II)$ derivative [35] consists of a central octahedral zinc(II) facially coordinated by two $\{(Me_3P)Pt(\mu\text{-}Cl)(\mu\text{-}SOP(OPr^i)_2\}_2$ ligands via two oxygen and one chlorine atoms, $\{Pt(\mu\text{-}\eta^2\text{-}SPO)_2(\mu\text{-}Cl)\}_2Zn$. The geometry at zinc(II) is distorted octahedral (ZnO_4Cl_2) and each platinum(II) is a square-planar, PtS_2ClP. The Pt...Zn separation is 3.88 Å and the Pt...Zn...Pt angle is 158º.

The structure of the $Pt(II)_2Na(I)$ derivative [36] is shown in Fig. 2. Each platinum(II) is coordinated by two nitrogen atoms of chelated 1,2-diaminopropane and two oxygen atoms of carboxylates, each one from different cantharidinate molecules (PtO_2N_2). The sodium(I) has a pseudo-octahedral structure (NaO_6).

Inspection of the data in Table 1 reveals that the platinum atoms are found in oxidation state (0) (x3) [21,23], +1 (x3) [15,17,19], +4 (x2) [11] and +2 in all remaining cases. The shortest Pt-M bond distances are: Pt(0)-Pb(II), 2.7325(6) and 2.7469(6) Å [21], Pt(I) – Hg(II), 2.669(1) (x2) [15]; Pt(II) – Hg(0), 2.544(5) (x2) [12] and Pt(IV) – Sn(II) 2.5386(6) and 2.5715(5) Å [11].

There are three examples, $[(NC)_2(\mu\text{-}\eta^2\text{-}dppm)_2(\mu\text{-}I)Pt_2HgI]Ch_2Cl_2.1.5H_2O$ [19], $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2BiCl_2]PF_6$ [31], and $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Zn(\eta^2\text{-}bpy)Cl]PF_6$ [31], which contain two crystallographically independent molecules that differ mostly by degree of distortion. All are examples of distortion isomerism [37].

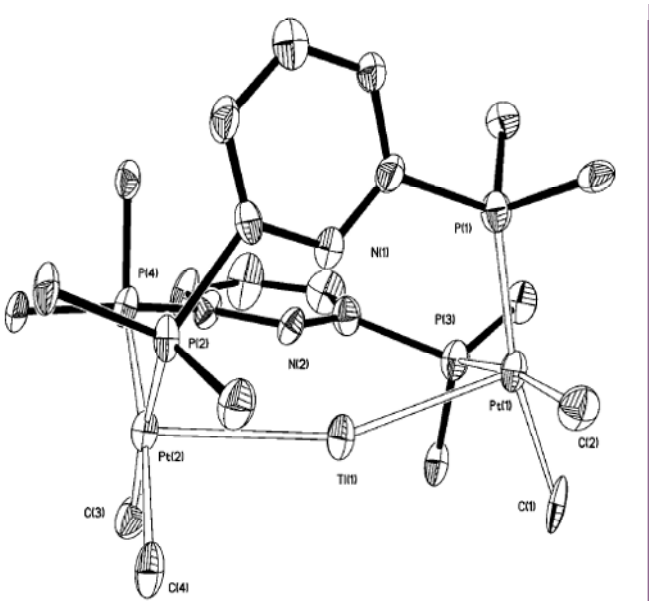

Figure 1. Structure of $[\{Me_2(\mu\text{-}\eta^2\text{-dppy})Pt\}_2Tl]^+$ for each phenyl ring in a Ph_2P group only the ipso carbon atom is shown [24].

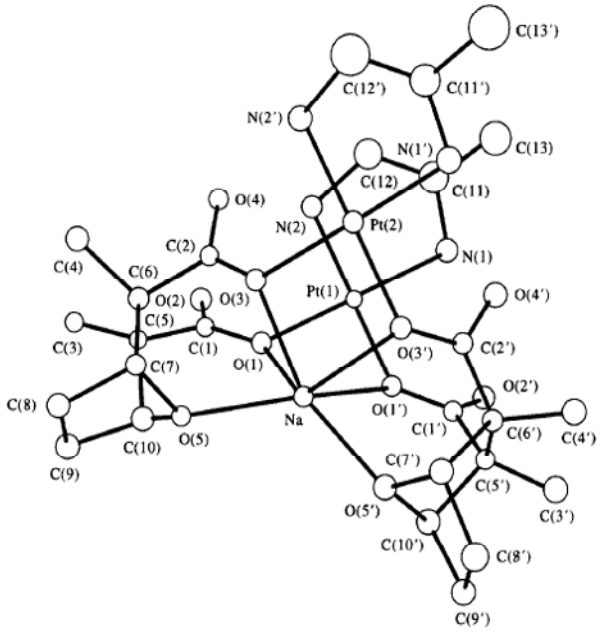

Figure 2. Structure of $[\{\eta^2\text{-1,2-pn})Pt\}_2(\mu\text{-can})_2Na]$ [36].

2.2. Pt_2M, M is transition metal

2.2.1. Pt_2M triangular

There are over fifty Pt_2M triangular derivatives and their crystallographic and structural data are summarized in Table 2. The triangular derivatives can be divided into four groups:

- with all metal-metal bonds
- only with Pt-M bonds
- only with Pt-Pt bond
- without metal-metal bonds (disulphide-bicapped).

2.2.1.1. Pt_2M metal-metal bonds

There are nineteen examples containing all metal-metal bonds. Their structures are listed in the order of an elongated sum of the Pt-M bond distances (Table 2A). There are several examples, M=Au [19,43,44], Fe [38,42], Co [39,40], Cu [41,51], Ru [45,46], Os [47a,52], Mo [47b,53], Ag [48-50] and W [54], which contain a triangle of the metal atoms. The shortest Pt-M as well as Pt-Pt bond distances are found in the orange $(OC)_2(\mu\text{-}\eta^2\text{-dppm})Pt_2Fe(CO)_4$

Table 1. Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
[{(η²Bu$^t_2$bpy)(Me)$_2$. ClPt}$_2$SnCl$_2$]. 2CH$_2$Cl$_2$ (yellow) (at 200 K)	tr P$\bar{1}$ 2	12.2220(5) 14.4855(6) 14.7589(7)	88.164(2) 84.218(2) 87.010(3)	Pt^{IV}N$_2$C$_2$ClSn Sn^{II}Cl$_2$Pt$_2$	η²N^b not given MeC not given Cl 2.458(2,1) Cl 2.413(2,12)	Sn 2.5386(6) 2.5451(5)	N,N^b not given Cl,Cl 96.93(9) Pt,Pt´ 136.34(2) Cl,Pt 104.28(6,1.4)	[11]
[{(η²-2,9-Me$_2$phen). (η²-mal)(H$_2$O). Pt}$_2$Hg](BF$_4$)$_2$ (yellow)	m P2$_1$/c 4	12.360(4) 12.296(5) 16.001(9)	 107.79(4) 	Pt^{II}N$_2$C$_2$OHg HgPt$_2$	η²N 2.15(1,1) η²C 2.03(2,1) H$_2$O 2.36(1)	Hg 2.5444(5)	N,N 77,2(4)^c C,C 40.9(7)^d N,C 120.9(7,3.0) N,O 90.9(4,1.6) C,O 85.8(5,2) N,Hg 89.2(3,5) C,Hg 94.2(4,3) O,Hg 179.5(3) Pt,Pt 180	[12]
[{(η²-Bu$^t_2$bpy)(Me). Cl$_2$Pt}$_2$Sn(Ph)Cl]. CH$_2$Cl$_2$ (yellow) (at 200 K)	m P2$_1$/n 4	18.5366(5) 13.9761(5) 21.8945(8)	 90.7519(2) 	Pt^{IV}N$_2$Cl$_2$C Sn Sn^{II}CClPt$_2$	η²N not given Cl 2.513(2,20) MeC not given PhC 2.165(7) Cl 2.397(2)	Sn 2.5715(5) 2.5725(5)	not given C,Cl 97.4(2) Pt,Pt´ 128.04(2) C,Pt 108.1(2,4.1) Cl,Pt 105.37 (5, 1.64)	[11]
[{(η²-dppen)(xylNC). Pt}$_2$Hg](PF$_6$)$_2$. CH$_2$Cl$_2$ (orange-yellow)	m P2$_1$/n 2	14.956(4) 12.395(2) 22.923(7)	 104.35(2) 	Pt^{II}P$_2$CHg HgPt$_2$	η^{5}P 2.260(4) 2.298(4) LNC 1.95(2)	Hg 2.615(1)	P,P 86.1(2)^c P,C 106.43(6) 167.7(6) P,Hg 86.6(1) 163.69(5) C,Hg 81.4(4) Pt,Pt 163.69(5)	[13] [14]
[{ (η²-dppp)(xylNC). Pt}$_2$Hg](PF$_6$)$_2$ (orange yellow)	m P2$_1$ 2	15.491(3) 22.575(5) 10.884(3)	 107.48(2) 	Pt^{II}P$_2$CHg HgPt$_2$	η²P 2.29(1,2) C 1.90(4,1)	Hg 2.635(2) 2.645(2)	P,P 93.2(4,3)^e P,C 96(1,2) 170(1,2) P,Hg 87.7(2,1) 173.0(3,2) C,Hg 83(1,1) Pt,Pt 178.41(9)	[13] [14]
[{(η²-dtbpe)(xylNC). Pt}$_2$Hg](PF$_6$)$_2$ (orange yellow)	m C2/c 4	19.489(6) 15.284(5) 25.804(6)	 116.34(2) 	Pt^{II}P$_2$CHg HgPt$_2$	η²P 2.307(4) 2.335(4) C 1.94(1)	Hg 2.6409(9)	P,P 86.6(2) P,C 98.8(4) 172.6(4) P,Hg 94.0(1) 173.2(1) P,Hg 78.7(4) Fe,Fe Pt,Pt 167.24(4)	[13] [14]
[{η³-dppp)Pt}$_2$. Hg(F$_3$CCOO)$_2$] (red brown)	or Cc2a 4	14.392(2) 19.950(1) 19.427(1)	 	Pt^{I}P$_2$CHgPt´ Hg^{II}O$_2$Pt$_2$	η³P 2.300(3,12) η³C 2.067(14)	Hg 2.6690(10) Pt´ 2.7608(7)	P,P 94.34(12)^e P,C 95.5(4) 170.1(4) P,Hg 97.60(9) 136.62(10) C,Hg 74.8(4) Hg,Pt´ 58.86(2) Pt,Pt´ 62.29(2)	[15]
(NBu$_4$)$_2$[{(C$_6$F$_5$)$_4$. Pt}$_2$Tl] (dark blue)	tr P$\bar{1}$ 2	15.088(5) 16.664(5) 21.641(5)	105.15(2) 96.91(2) 114.01(2)	Pt^{II}C$_4$Tl Tl^{III}Pt$_2$	C not given	Tl 2.698(1) 2.708(1)	C,C not given Pt,Pt 179(1)	[16]
[{(η ²-dppm)ClPt}$_2$. HgCl$_2$]^f (orange)	tr P$\bar{1}$ 2	11.587(3) 22.156(5) 23.036(5)	65.53(2) 76.53(2) 84.30(2	Pt^{I}P$_2$ClHgPt´ Hg^{II}Cl$_2$Pt$_2$ Pt^{I}P$_2$ClHgPt´ Hg^{II}Cl$_2$Pt$_2$	η²P 2.300(4,11) Cl 2.343(4,7) Cl 2.447(5,2) η²P 2.301(4,10) Cl 2.334(4,4) Cl 2.429(4,12)	H g 2.6991(8) 2.7097(8) Pt´ 2.7361(9) Hg 2.7122(8) 2.7133(7) Pt 2.7119(8)	P,P 174.3(1,1) P,Cl 87.4(1,1.7) Hg,Pt 59.75(3,33) Cl,Cl 103.7(1) Pt,Pt´ 60.78(2) P,P 175.2(1,8) P,Cl 88.6(1,2.4) Hg,Pt´ 60.02(2,6) Cl,Cl 106.0(1) Pt,Pt 59.96(2)	[17]

Continued Table 1. Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
$(NBu_4)[(C_6F_5)_3Pt.(\mu\text{-}Pb)(\mu\text{-}OH).Pt(C_6F_5)_3]$ (yellow)	tr P$\bar{1}$ 2	10.707(4) 15.863(6) 17.828(5)	104.57(3) 98.97(3) 100.05(3)	$Pt^{II}C_3OPb$ $Pb^{II}Pt_2$	C 1.982(16,3) 2.076(14,15) μHO 2.128(9,5)	Pb 2.701(1) 2.712(1) O 110.4(4)	C,C 91.0(6,3.1) 172.7(6,2) C,μO 88.7(5,4.4) 173.6(5,7) C,Pd 96.0(4,6.7) μO,Pd 84.6(2,2) Pt,Pt 80.5(1)	[18]
$(NBu_4)[(C_6F_5)_3Pt.(\mu\text{-}Pb)(\mu\text{-}Cl)Pt.(C_6F_5)_3]$ (yellow)	m C2/c 8	32.121(6) 17.828(4) 19.389(4)	 93.37(3) 	$Pt^{II}C_3ClPb$ $Pb^{II}Pt_2$	C 2.017(10,7) 2.070(11,12) μCl 2.426(2,5)	Pb 2.721(1) 2.729(1) Cl 99.03(9)	C,C 89.4(4,1.2) 173.9(4,1.0) C,μCl 90.3(3,5.1) 170.8 (3,2) C,Pb 95.8(3,8.4) μCl,Pb 87.77(6,19) Pt,Pt 85.25(3)	[18]
$[(NC)_2(\mu\text{-}\eta^2\text{-}dppm)_2.(\mu\text{-}I)Pt_2HgI].CH_2Cl_2.1.5H_2O^f$ (orange) (at 130 K)	tr P$\bar{1}$ 4	15.311(3) 16.132(5) 24.911(6)	82.99(2) 81.02(2) 89.80(2)	$PtP_2ClHgPt$ $Hg^{II}IPt_2$ $PtP_2ClHgPt$ $Hg^{II}IPt_2$	$\mu\eta^2$P 2.308(8,6) NC 1.95(4,5) μI 2.913(3,3) I 2.655(2) $\mu\eta^2$P 2.310(7,13) NC 2.00(3,3) μI 2.916(3,9) I 2.656(3)	Hg 2.700(2) 2.725(2) Pt 2.819(2) I not given Hg 2.700(2) 2.729(2) Pt ´2.823(2) I not given	P,P 172.2(3,1) C,μI 121.3(8,3.2) μI,Hg 119.8(1,4) μI,Pt 61.2(1,0) Hg,Pt 58.7(1,4) I,Pt 148.6(1,2.8) Pt,Pt 62.6(1) P,P 171.9(3,1) C,μI 119.2(9,2.8) μI,Hg 119.7(1,8) μI,Pt 61.0(1,4) Hg,Pt 58.7(1,5) I,Pt 148.6(1,1.5) Pt,Pt 62.7(1)	[19]
$(NBu_4)_2[(C_6F_5)_6(\mu\text{-}OH).Pt_2Hg(C_6F_5)]$ (yellow) (at 233 (1) K)	m C2/c 4	19.787(6) 21.495(6) 18.242(5)	 96.18(3) 	$Pt^{II}C_3OHg$ $Hg^{II}CPt_2$	C 2.02(1) 2.09(1,1) μHO 2.074(6) C 2.09(2)	Hg 2.718(1,0) O 116.0(5)	C,C 90.4(5,1.6) 176.1(5) μO,Hg 81.6(3) C,Pt 139.7(1) Pt,Pt 80.7(1)	[20]
$[(\mu\text{-}\eta^2\text{-}dpphen)_3Pt_2Pb].(NO_3)_2Pb(NO_3)_2.4DCE.MeOH$ (brown)	tr P$\bar{1}$ 2	18.2425(3) 25.6650(4) 29.2485(6)	64.932(1) 79.399(1) 78.724(1)	Pt^0P_3Pb $Pb^{II}Pt_2$	$\mu\eta^2$P not given	Pb 2.7325(6) 2.7469(6)	not given not given	[21]
$(NBu_4)_2[\{(C_6F_5)_4.Pt\}_2Pb].0.8CHCl_3$ (green-yellow)	tr P$\bar{1}$ 4	15.088(13) 16.697(13) 21.645(6)	105.64(6) 97.08(6) 113.48(6)	$Pt^{II}C_4Pb$ $Pb^{II}Pt_2$	C 2.072(17,26)	Pb 2.769(2) 2.793(2)	not given Pt,Pt 178.6(1)	[22]
$[(\mu\text{-}\eta^2\text{-}dpphen)_3Pt_2.Tl]NO_3$ (red)	m C2/c 8	33.6379(5) 14.8130(1) 41.9035(6)	 107.743(1) 	Pt^0P_3Tl Tl^IPt_2	$\mu\eta^2$P 2.281(4,17)	Tl 2.7907(9) 2.7919(9)	P,P 118.1(1,6.4) P,Tl 97.9(1,3.1) Pt,Pt 175.27(3)	[23]
$[(\mu\text{-}\eta^2\text{-}dpbpy)_3.Pt_2Tl]NO_3$ (red)	rh R$\bar{3}$c 6	19.3694(1) 51.9258(2)	 	Pt^0P_3Tl Tl^IPt_2	$\mu\eta^2$P 2.312(1)	Tl 2.7953(2)	P,P 117.68(1) P,Tl 98.83(3) Pt,Pt 180	[23]
$[\{Me_2(\mu\text{-}\eta\ ^2\text{-}dppy).Pt\}_2.Tl]ClO_4.1.5thf$ (yellow)	tr P$\bar{1}$ 2	13.006(2) 14.218(3) 21.486(4)	71.709(3) 81.218(4) 64.587(4)	$Pt^{II}C_2P_2Tl$ Tl^IPt_2	MeC 2.060(12,3) 2.113(10,16) $\mu\eta^2$P 2.314(3,8) 2.340(3,13)	Tl 2.7961(/7) 2.8090(7)	C,C 82.8(4,5) P,P 100.34(9,1,28) C,P 88.6(3,3.3) 170.2(3,4.5) C,Tl 90.4(3,2.3) P,Tl 91.98(6,4.48) Pt,Pt 157.88(2)	[24]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}O)_2.Li(\eta^2\text{-}F_2BF_2)].BF_4.0.5tol$ (yellow) (at 183 K)	m C2/c 4	20.469(8) 18.085(9) 18.152(8)	 90.34(6) 	$Pt^{II}O_2P_2$ $Li^IF_2O_2$	μ_3O 2.028(6,10) Ph_3P 2.252(3,10) F 1.89(2,0) μ_3O 2.08(2,0)	Li not given O 80.3(4,2) Pt 2.969(1) O 94.1(3)	O,O 77.4(3) P,P 101.9(2,1.6) O,P 90.2(2,6.1) 166.4(2,6) F,F 75.3(9)[a] F,O 113.3(4) 154.7(4)	[25]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2.GaCl_2][GaCl_4]$ (cream white)	m P2$_1$/c 4	14.133(3) 17.399(3) 29.126(6)	 94.75(2) 	$Pt^{II}S_2P_2$ $Ga^{III}S_2Cl_2$	μ_3S 2.389(2,8) Ph_3P 2.292(2) μ_3S 2.294(2,3) Cl 2.185(3,4)	Ga 3.041(1) S 81.0(1) Pt 3.220(1) S 84.8(1)	S,S 79.8(1,2) P,P 98.8(1,2) S,P 90.7(1,2.0) S,S 83.9(1) Cl,Cl 104.0(1) S,Cl 117.3(1,2.1)	[26]

Continued **Table 1.** Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
$(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $InCl_3$ (yellow)	m P2/c 4	26.273(5) 11.955(2) 21.257(4)	 92.96(3) 	$Pt^{II}S_2P_2$ $In^{III}Cl_3S_2$	μ_3S 2.359(2,8) Ph_3P 2.303(2,3) Cl 2.131(5) 2.597(7,69) μ_3S 2.614(2)	In 3.341(3) S not given Pt 3.253(2) S not given	S,S 79.9(1) P,P 99.7(1) S,P 90.2(1,5) 169.9(1,6) Cl,Cl 82.9(2) 106.2(3,3.2) S,S 70.8(1)	[26]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Tl]PF_6$ (yellow)	m $P2_1/n$ 2	18.128(4) 10.544(2) 18.348(4)	 107.37(3) 	$Pt^{II}S_2P_2$ $Tl^{I}S_2$	μ_3S 2.368(3,12) Ph_3P 2.303(3,9) μ_3S 2.764(3)	Tl 3.379(1) S 82.0(1,2) Pt 3.293(2) S 88.1(1)	S,S 82.6(1) P,P 97.0(1) S,P 87.4(1) 175.5(1) S,S 68.9(1) Pt,Pt 58.3(1)	[27]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Sn(Ph)Cl_2]$. PF_6.2.5$CHCl_3$ (pale yellow)	tr P$\bar{1}$ 2	13.6794(2) 16.1453(1) 21.8422(1)	108.944(1) 91.992(1) 90.339(1)	$Pt^{II}S_2P_2$ $Sn^{IV}Cl_2S_2C$	μ_3S 2.342(3,3) 2.380(3,9) Ph_3P 2.289(4,1) 2.315(3.7) Cl 2.402(4,13) μ_3S 2.537(3,22) PhC 2.112(14)	Sn 3.244 S 83.1(1,7.6) Pt 3.246 S 86.9(1,2)	S,S 79.9(1,8) P,P 100.2(1,6) S,P 89.3(1,2.2) 168.8(1,1.4) Cl,Cl 89.16(13) S,S 73.35(10) Cl,C 103.1(4,3.0) Cl,S 89.9(1,1.4) 152.17(12) S,C 110.2(4,4.2)	[28]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Sn(Me(Cl_2]PF_6$ (pale-yellow)	m $P2_1/c$ 4	19.8509(4) 19.3975(4) 17.8759(4)	 91.769(1) 	$Pt^{II}S_4P_2$ $Sn^{IV}Cl_2S_2C$	μ_3S 2.362(1,28) Ph_3P 2.282(1,1) 2.309(1,30) Cl 2.396(2,30) μ_3S 2.562(1,50) MeC 2.125(6)	Sn 3.276 S 83.4(1,6.7) Pt 3.288 S 88.1(-,1)	S,S 79.33(5,51) P,P 98.95(5,67) S,P 91.28(5,1.21) 170.02(5,13) Cl,Cl 93.85(5) S,S 72.07(5) Cl,C 99.8(2,5.5) Cl,S107.55(6,6.59) 158.79(7) S,C 96.3(2)	[28]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Sn(Me)_2Cl]PF_6$ (pale yellow)	m $P2_1/c$ 4	20.045(2) 19.7353(1) 17.9958(1)	 90.440(1) 	$Pt^{II}S_2P_2$ $Sn^{IV}C_2S_2Cl$	μ_3S 2.363(2,13) Ph_3P 2.296(2,4) 2.322(2,0) MeC 2.149(13,5) μ_3S 2.597(2,45) Cl 2.489(6)	Sn 3.286 S 82.9(1,3.8) Pt 3.372 S 91.0(-,2)	S,S 78.74(8,5) P,P 99.77(8,96) S,P 90.09(7,94) 168.17(8,26) C,C 107.1(7) S,S 70.47(10) C,Cl 94.5(5,9) C,S 99.1(5,1.0) 126.3(6,4.7) Cl,S 86.6(2) 157.0(2)	[28]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Sn(CH_2Ph)_2Br]$. PF_6.0.5$CHCl_3$ (pale yellow)	m $P2_1/n$ 4	13.9114(2) 19.3113(2) 32.5520(1)	 90.743(1) 	$Pt^{II}S_2P_2$ $Sn^{IV}C_2S_2Br$	μ_3S 2.374(3,7) Ph_3P 2.309(3,8) 2.326(3,8) C 2.166(17,5) μ_3S 2.524(4) 2.761(3) Br 2.612(2)	Sn 3.409 S 85.6(1,4.5) Pt 3.263 S not given	S,S 79.17(11,14) P,P 100.46(13,42) S,P 91.9(1,4) 170.7(1,3) C,C 117.2(7) S,S 69.70(10) C,S 100.1(4,15.7) C,Br 98.0(5,4.5) S,Br 89.89(10) 159.08(10)	[28]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Pb(\eta^2\text{-}O_2NO)]PF_6$ (yellow)	m $P2_1/c$ 4	23.240(8) 13.191(7) 23.650(6)	 109.63(2) 	$Pt^{II}S_2P_2$ $Pb^{II}O_2S_2$	μ_3S 2.358(2,10) Ph_3P 2.299(2) η^2O 2.403(8) 2.637(10) μ_3S 2.641(3) 2.766(3)	Pb 3.361(2,33) S not given Pt 3.290(2) S not given	S,S 81.2(1) P,P 98.9(1) S,P 89.2(1,4.0) O,O 49.4(3)[g] S,S 69.2(1) O,S 92.9(3,7.6) 142.3(2)	[29]

Continued **Table 1.** Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Pb(\eta^2\text{-}O_2NO)_2]$ (yellow)	m $P2_1/c$ 4	23.045(7) 13.326(4) 24.013(10)	 111.63(3)	$Pt^{II}S_2P_2$ $Pb^{II}O_4S_2$	μ_3S 2.351(3,17) Ph_3P 2.296(4) η^2O 2.642(16,68) 2.871(16,81) μ_3S 2.718(4,26)	Pb 3.389(2,44) S not given Pt 3.266(2) S not given	S,S 81.2(1,3) P,P 100.7(1,7) S,P 89.1(1,2.9) O,O 40.8(6,5.6)[a] S,S 68.5(1) O,S 94.9(5,9.8) 146.0(4)	[29]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}BiCl_3].CH_2Cl_2$ (orange)	tr $P\bar{1}$ 2	12.081(2) 15.225(3) 20.868(4)	74.32(3) 86.50(3) 80.82(3)	$Pt^{II}S_2P_2$ $IBr^{III}Cl_3S_2$	μ_3S 2.363(3,19) Ph_3P 2.305(3,15) Cl 2.610(5) 2.719(4,34) μ_3S 2.639(3) 2.884(3)	S 87.2(1,6)	S,S 80.2(1,2) P,P 100.0(1,1.2) S,P 90.0(1,1.9) 171.4(1) Cl,Cl 87.8(1,3) 149.1(1) S,S 66.6(1) Cl,S 99.8(1,8.4) 160.1(1)	[30]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}BiCl_2]PF_6$ (orange)	m C2/c 4	21.264(4) 19.292(4) 17.303(3)	 93.11(3)	$Pt^{II}S_2P_2$ $Bi^{III}Cl_2S_2$	μ_3S 2.321(7,10) 2.415(7,24) Ph_3P not given Cl 2.520(4,56) μ_3S 2.626(7) 2.758(7)	Bi 3.367(1,64) S 86.9(2,.2)	S,S 86.6(2,51) P,P 97.6(1) S,P 90.8(2,3.1) Cl,Cl 109.1(2) S,S 70.1(2) Cl,S 104.6(2,1.8) 125.3(2,7.7)	[30]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Zn(\eta^2\text{-}bpy)Cl].PF_6$[f] (yellow) (at 183 K)	tr $P\bar{1}$ 4	14.5319(2) 20.0832(2) 29.2213(3)	83.434(1) 88.522(1) 83.281(1)	$Pt^{II}S_2P_2$ $Zn^{II}N_2S_2Cl$ $Pt^{II}S_2P_2$ $Zn^{II}N_2S_2Cl$	μ_3S 2.364(2,14) Ph_3P 2.293(2,6) 2 .314(2,2) η^2N 2.190(7,19) μ_3S 2.491(2,41) Cl 2.299(2) μ_3S 2.363(2,14) Ph_3P 2.294(2,12) 2.311(2,0) η^2N 2.169(7,25) μ_3S 2.495(2,70) Cl 2.283(2)	Zn 3.205(1,56) S not given Pt 3.252(2) S not given Zn 3.202(1,64) S not given Pt 3.249(2) S not given	S,S 80.21(6,14) P,P 100.55(8,2.63) S,P 89.70(7,4.92) 169.27(8,5.18) N,N 74.1(3)[c] S,S 75.35(7) N,Cl 99.5(2,3.9) S,Cl 113.59(8,7.9) S,S 80.40(6,14) P,P 99.76(8,58) S,P 89.93(7,3.53) 169.92(7,3.4) N,N 75.6(3)[c] S,S 75.32(6) N,Cl 99.6(2,3.8) S,Cl 115.41(8,5.37)	[31]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Cd(\eta^2\text{-}bpy)Cl].PF_6$[f] (yellow) (at 183 K)	tr $P\bar{1}$ 4	14.5256(5) 20.1188(7) 29.3002(11)	83.110(1) 88.390(1) 82.842(1)	$Pt^{II}S_2P_2$ $Cd^{II}N_2S_2Cl$	μ_3S 2.359(2,14) Ph_3P 2.287(2,5) 2.301(2,7) η^2N 2.374(6,0) μ_3S 2.626(2,1) Cl 2.468(2)	Cd 3.270(1,44) S not given Pt 3.274(3) S not given	S,S 81.76(5,15) P,P 100.59(6,2.24) S,P 88.89(6,4.71) 170.13(6,5.09) N,N 68.5(2)[c] S,S 72.05(5) N,Cl 99.6(1,4.7) S,Cl 115.64(6,6.29)	[31]
				$Pt^{II}S_2P_2$ $Cd^{II}N_2S_2Cl$	μ_3S 2.360(2,13) Ph_3P 2.283(2,12) 2.301(2,4) η^2N 2.366(6,24) μ_3S 2.621(2,35) Cl 2.444(2)	Cd 3.270(1,4) S not given Pt 3.257(3) S not given	S,S 82.00(5,4) P,P 99.94(7,48) S,P 89.03(6,3.67) 170.61(6,3.79) N,N 69.6(2)[c] S,S 72.40(5) N,Cl 99.3(1,4.7) S,Cl 119.66(7,3.76)	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Hg(PPh_3)](PF_6)_2\cdot H_2O$ (yellow)	m $P2_1/n$ 4	18.1038(3) 27.8444(1) 20.295(3)	 92.456(1)	$Pt^{II}S_2P_2$ $Hg^{II}S_2P$	μ_3S 2.389(2,34) Ph_3P 2.311(2,17) μ_3S 2.428(2) 2.694(2) Ph_3P 2.402(3)	Hg 3.194(5,5) S 80.30(7,2.8) Pt 3.306(5) S 87.60(7,27)	S,S 82.32(7,12) P,P 98.08(9) P,S 89.85(8,1.75) 171.80(9,1.52) S,S 75.54(7) S,P 116.65(8) 166.96(9)	[32]

Continued **Table 1.** Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromophore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2.HgCl_2]CH_2Cl_2$ (yellow)	tr P$\bar{1}$ 2	16.4366(10) 17.6321(3) 18.2643(3)	114.73(1) 102.828(10) 98.01(1)	$Pt^{II}S_2P_2$ $Hg^{II}Cl_2S_2$	μ_3S 2.362(2,20) Ph_3P 2.290(2,11) Cl 2.484(4,3) μ_3S 2.630(2,116)	Hg 3.302(7,6) S not given Pt 3.254(7) S not given	S,S 81.56(8) P,P 99.61(8) S,P 89.1(1,2.9) Cl,Cl 106.44(4) S,S 71.86(7) Cl,S 119.0(1,1.0)	[32]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2.Hg(Ph)]2CH_2Cl_2$ (yellow)	tr P$\bar{1}$ 2	13.6833(2) 17.5864(3) 19.5672(2)	82.352(1) 88.935(1) 81.599(1)	$Pt^{II}S_2P_2$ $Hg^{II}S_2C$	μ_3S 2.351(1,5) 2.388(1,20) Ph_3P 2.286(1,16) 2.293(1,2) μ_3S 2.4079(12) 2.9286(12) PhC 2.081(5)	Hg 3.296 S 81.8(-,12.6) Pt 3.268 S 87.2(-,8)	S,S 82.42(4,32) P,P 99.21(4,58) S,P 88.11(4,2.95) 168.62(2,1.81) S,S 70.85(3) S,C 113.00(15) 174.59(16)	[28]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}Se)_2.Sn(Me)I_2Cl]PF_6$ (light brown)	m P2$_1$/c 4	20.2150(3) 19.524(1) 18.0565(3)	 91.88(1) 	$Pt^{II}Se_2P_2$ $Sn^{IV}C_2SeCl$	μ_3Se 2.478(-,25) 2.488(1,4) Ph_3P 2.293(1,1) 2.317(1,4) MeC 2.137(4,1) μ_3Se2.6316(6) 2.7943(5) Cl 2.4885(14)	Sn not given Se 83.13(1,6.2) Pt not given Se 88.52(1,20)	Se,Se 79.70(1,45) P,P 99.58(4,82) Se,P 90.41(3,2.2) 169.57(3,2.54) C,C 112.1(2) Se,Se 71.743(15) C,Cl 93.71(17.51) Se,Cl 87.55(4) 158.03(5)	[33]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}Se)_2.Sn(Bu_2)Cl]PF_6$ (light brown)	tr P$\bar{1}$ 2	12.337(2) 16.102(5) 21.258(5)	86.54(2) 86.82(2) 87.80(2)	$Pt^{II}Se_2P_2$ $Sn^{IV}C_2Se_2Cl$	μ_3Se 2.463(-,3) 2.493(-,4) Ph_3P 2.287(2,2) 2.308(2,7) BuC 2.132(9,9) μ_3Se 2.4599(9) 2.4897(9) Cl 2.475(3)	Sn not given Se 84..90(3,4) Pt not given Se 86.92(3,66)	Se,Se 79.80(3,14) P,P 98.79(6,23) Se,P 90.94(5,2.86) 169.03(5,2.92) C,C 116.7(5) Se,Se 69.93(3) C,Cl 96.3(4,1.6)	[33]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}Se)_2.Sn(Bu)Cl_2]PF_6.3.5CHCl_3$ (pale yellow)	tr P$\bar{1}$ 2	14.4249(2) 16.5335(2) 21.0858(3)	69.018(1) 84.323(1) 86.547(1)	$Pt^{II}Se_2P_2$ $Sn^{IV}Cl_2Se_2C$	μ_3Se 2.4852(8,2) 2.489(-,17) Ph_3P 2.302(2,8) 2.319(2,1) Cl 2.422(3,35) μ_3Se 2.5993(11) 2.809(1) BuC 2.161(11)	Sn not given Se 83.61(3,5.4) Pt not given Se 86.90(3,8)	Se,Se 80.12(3,33) P,P 100.14(8,1.04) Se,P 89.93(7,2.13) 169.35(7,3.41) Cl,Cl 94.63(12) Se,Se 72.46(3) Cl,C 99.7(4,4.0) Se,C 96.7(3) 144.0(4)	[33]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}Se)_2.Pb(\eta^2\text{-}O_2NO)_2].CH_2Cl_2$ (brown)	tr P$\bar{1}$ 2	12.1770(2) 16.8986(3) 17.5281(3)	75.202(1) 87.163(1) 89.219(1)	$Pt^{II}Se_2P_2$ $Pb^{II}O_4Se_2$	μ_3Se 2.462(1,9) 2.477(1,9) Ph_3P 2.292(3) η^2O 2.559(9) 2.844(8,54) μ_3Se 2.820(1,38)	not given not given not given	Se,Se 81.8(4,30) P,P 99.49(9,10) Se,P 89.31(7,3.35) O,O 45.0(3,3)[a] Se,Se 69.99(3)	[34]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}Se)_2.CdCl_2].CH_2Cl_2.2H_2O$ (bright yellow)	m P2/n 2	17.2097(12) 11.8079(9) 17.6063(12)	 105.918(2) 	$Pt^{II}Se_2P_2$ $Cd^{II}Cl_2Se_2$	μ_3Se 2.4595(7) 2.4917(7) Ph_3P 2.2727(17) 2.2885(18) Cl 2.438(2,0) μ_3Se 2.6852(10)	Cd 3.3235(8,0) Se 80.06(2,3) Pt not given Se 86.97.7(2)	Se,Se 83.08(3) P,P 99.13(6) Se,P 88.91(5,2.2) 171.84(5,2.2) Cl,Cl 113.20(14) Se,Se 75.38(4) Cl,Se115.83(7,1.7)	[34]
$[\{(Me_3P)Pt(\mu\text{-}Cl).((\mu\text{-}\eta^2\text{-}SOP(OPr^i)_2)_2\}_2\text{-}Zn]CH_2Cl_2$	m C2/c 4	25.13(/2) 10.866(7) 27.85(2)	 119.83(5) 	$Pt^{II}S_2ClP$ $Zn^{II}O_4Cl_2$	$\mu\eta^2$S 2.332(5,2) μCl 2.392(5) Me_3P 2.212(5) $\mu\eta^2$P 2.277(9) 2.318(4) μCl 2.802(5)	Zn 3.88 Cl 96.3(2)	S,Cl 88.9(2,1.7) S,P 91.1(2,3.0) O,O 95.3(4,5.5) 164.5(5) Cl,Cl 103.0(2) O,Cl 84.1&(3,1.6) 172.2(3)	[35]

Continued **Table 1.** Crystallographic and structural data for heterotrinuclear platinum compounds, Pt_2M (M = non-transition metal)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref.
[{(η^2-1,2-pn)Pt}$_2$.(μ-can)$_2$Na].4H$_2$O (pale yellow)	m $P2_1/a$ 4	13.297(3) 19.089(4) 15.999(2)	 103.29(2) 	$Pt^{II}O_2N_2$ Na^IO_6	μO 2.033(5,11) 2.054(6,2) η^2N 2.059(7,13) 2.092(8,8) O 2.296(6,5) μO 2.369(6,1) 2.422(7,20)		O,O 83.8(3,2.2) N,N 85.8(3,2)[c] O,N 94.9(3,2.8) 174.3(3,1.9) O,O 121.0(2) μO,μO 73.2(2,4.9) 115.0(3,5) O,μO 76.2(2,1.3)[e] 139.5(2,3.2)	[36]

Footnotes:
a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Five-membered metallocyclic ring.
d. Three-membered metallocyclic ring.
e. Six-membered metallocyclic ring.
f. There are two crystallographically independent molecules.
g. Four-membered metallocyclic ring.

Table 2. Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: Pt_2M, METAL-METAL BONDS								
(OC)$_2$(μ-η^2-dppm).Pt$_2$Fe(CO)$_4$ (orange)	m $P2_1/c$?	13.517(3) 11.326(1) 24.028(6)	 59.70(2) 	PtCPFePt FeC_4Pt_2	OC[b] 1.87(2,0) $\mu\eta^2$P 2.248(6,4) OC 1.77(3,3)	Fe 2.541(3,0) Pt 2.581(1)	C,Fe[b] 105(1,0) C,Pt 165(1,0) P,Pt 95.0(1,1.3) Fe,Pt 59.48(8,1) C,C 100(1,6) 144(1) Pt,Pt 61.09(9)	[38]
(Ph$_3$P)$_2$(μ-PPh$_2$)Pt$_2$.(μ-CO)$_2$Co(CO).(PPh$_3$) (green)	tr P$\bar{1}$ 2	14.807(8) 15.051(8) 14.047(8)	93.14(5) 108.75(4) 94.55(5)	Pt^IP_2CCoPt CoC_3PPt_2	Ph_3P 2.255(3,10) μP 2.255(3,3) μOC 2.117(14,18) OC 1.80(2) μOC 1.85(1,3) Ph_3P 2.163(4)	Co 2.557(2,17) C 80.0(5,6) Pt 2.664(1) P not given	P,μP 110.7(1,1.6) P,C 98.6(4.3) μP,C 146.6(3,2.4) μP,Co 112.1(1,6) μP,Pt 53.80(8,11) Co,Pt 58.60(4,63) μC,μC 119.1(6) μC,P 94.1(5,6) μC,Pt 54.6(4,1.1) 108.6(4,1.0) Pt,Pt 62.79(4)	[39]
[(Ph$_3$P)$_2$(μ-PPh)$_2$)Pt$_2$.(μ-CO)$_2$Co(CO)$_2$].2tol (green)	tr P$\bar{1}$ 2	11.791(4) 13.471(6) 18.887(9)	106.654(4) 95.844(3) 92.983(4)	Pt^IP_2CCoPt CoC_4Pt_2	PhC 2.253(2,1) μP 2.263(2,2) μOC 2.10(1,2) OC 1.78(1,4) μOC 1.86(1,0)	Co 2.560(2,14) C 80.5(4,2) Pt 2.655(1) P 71.86(8)	P,μP 112.94(9,28) P,C 96.6(3,1.2) P,Pt 166.46(7,19) μP,Pt 54.1(1,1) C,Co 45.8(3,2) C,Pt 94.5(3,2.5) Co,Pt 58.77(3,51) C,C 104.41(5) μC,μC 107.7(5) Pt,Pt 62.46 (4)	[40]
[(Ph$_3$P)$_2$(μ-PPh$_2$.(μ-o-C$_6$H$_4$PPh$_2$)Cu.(PPh$_3$)]PF$_6$ CH$_2$Cl$_2$ (orange-yellow)	tr P$\bar{1}$ 2	13.319(2) 17.472(2) 18.380(2)	84.59(1) 80.87(1) 86.56(1)	PtP_2CCuPt PtP_3CuPt CuC_2PPt_2	Ph_3P 2.278(6) μP 2.248(5) μC 2.11(2) Ph_3P 2.302(5) μP 2.292(5) μLP 2.283(5) C 2.87(1) μC 2.52(1) Ph_3P 2.180(6)	Cu 2.565(3,30) C not given P t 2.657(1) P 113.8(4)	P,C 102.0(3) P,Pt 162.8(1) μP,Pt 55.0(1) μP,Cu 96.2(1) Cu,Pt 59.9(1) μP,Cu 93.5(2) μP,Pt 53.4(1) Cu,Pt 57.7(1) P,Pt 139.0(1) 151.5(2) Pt,Pt 62.4(1)	[41]

Continued **Table 2.** Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
{ $(PhO)_3P\}_3(OC)Pt_2$. $Fe(CO)_4$ (orange)	tr P$\bar{1}$ 2	22.80(2) 12.31(1) 10.55(1)	105.2(1) 78.0(1) 88.6(1)	PtP_2FePt	P 2.210(9,8)	Fe 2.566(6,17) Pt 2.633(1)	P,P 100.1(3) P,Fe 105.0(3) P,Pt 163.5(3) Fe,Pt 58.5(1)	[42]
				$PtCPFePt$	OC 1.94(4) P 2.236(8)		C,P 97.4(9) C,Pt 101.7(8) P,Pt 160.9(3) Fe,Pt 59.8(1)	
				FeC_4Pt_2	OC 1.78(4,4)		Pt,Pt 61.7(1)	
$[(NC)_2(\mu\text{-}\eta^2\text{-dppm})_2$. $Pt_2AuCl]CH_2Cl_2$ (yellow) (at 130 K)	tg $P4_3$ 4	20.933(5) 14.381(6)		Pt^tP_2CAuPt	$\mu\eta^2$P 2.237(9,0) 2.346(9,13) NC 1.976(37,13)	Au 2.640(2,8) Pt 2.821(2)	P,P 176.3(3,2.8) P,C 88.7(11,5.6) P,Au 90.7(2,4.1) P,Pt 91.6(2,3.7) Au,Pt 57.8(1,3)	[19]
				Au^tClPt_2	Cl 2.247(11)		C,Pt,147.3(3,8.8) Pt,Pt 64.6(1)	
$(Bu^tC{\equiv}C)_2(\mu\text{-}\eta^2$-dppm)$_2$.$Pt_2AuI$ (yellow)	or $Pna2_1$ 4	29.053(4) 16.131(3) 13.956(3)		Pt^tP_2CAuPt	$\mu\eta^2$P 2.281(6,9) C 2.01(3,1)	Au 2.658(2,3) Pt 2.837(1)	P,P 17659(3,7) P,C 88.5(7,3.8) P,Au 91.2(2,2.1) P,Pt 91.3(2,4.3) Au,Pt 57.8(1,1)	[43]
				Au^tIPt_2	I 2.580(2)		I,Pt 147.8(2,3 Pt,Pt 64.5(1)	
$[(cy_3P)_2(xylNC)_2$. $(\mu\text{-}SO_2)Pt_2Au(Pcy_3)]$. 0.5thf (yellow)	m $P2_1/c$ 4	18.545(4) 21.662(5) 41.353(9)	92.32(2)	$Pt^tCSPAuPt$	C 1.94(6,1) μS 2.23(4,2) P 2.26(4,2)	Au 2.711(7,6) Pt 2.704(8)	S,Pt 52.7(9,8) P,Pt 149.1(9,2.2) P,Au 143.2(8,2.6) Au,Pt 60.1(2,2)	[44]
				$AuPPt_2$	P 2.27(4)		P,Pt 146.3(9,8) Pt,Pt 59.8(2)	
$(Ph_2MeP)_2(\mu\text{-CO})$. $Pt_2(\mu\text{-}CO)_2Ru$. $(CO)_2(PMePh_2)$ (golden)	tr P$\bar{1}$ 2	10.694(3) 22.424(7) 8.938(2)	83.41(2) 90.02(2) 92.42(2)	PtC_2PRuPt	μOC 2.08(2,1) P 2.26(1,2)	Ru 2.718(2,11) C 80.2(8,1.2) Pt 2.647(2) C 79.0(11)	μC,P 99.0(9,1.9) μC,Pt 50.6(9,5) μC,Ru 50.7(7,1.5) Ru,Pt 60.86(5,41)	[45]
				RuC_4PPt_2	OC 1.92(3,2) μOC 2.13(2,6) P 2.40(1)		C,C 91.5(11) μC,P 90.1(7,1.8) μC,Pt 49.0(6,4) Pt,Pt 58.28 (5)	
$[(Ph_3P)_2(\mu\text{-CO})Pt_2$. $(\mu\text{-}CO)_2Ru(CO)_2$. $(PPh_3)].2C_6H_6$ (yellow)	m $P2_1/c$ 4	11.868(4) 18.647(8) 29.24(1)	98.35(5)	PtC_2PRuPt	μOC 2.06(2,4) P 2.269(2,1)	Ru 2.730(2,9) C 81.6(7,5 P t 2.661(2) C 80.2(7)	μC,P 100.2(6,5) μC,Pt 49.9(6,2) μC,Ru 50.3(6,2) Ru,Pt 60.83(3,13)	[46]
				RuC_4PPt_2	OC 1.90(2,3) μOC 2.12(2,1)		Pt,Pt 58.34(3)	
$[(Ph_3P)_2(\mu\text{-CO})Pt_2$. $(\mu\text{-}CO)_2Ru(CO)_2$. $(PPh_3)]$ (yellow)	tr P$\bar{1}$ 2	15.893(5) 15.400(5) 12.651(4)	57.04(2) 77.09(3) 84.10(3)	PtC_2PRuPt	μOC 2.053(10,8) P 2.262(3,1)	Ru 2.737(2,4) C 81.4(2,7) Pt 2.651(1) C 80.6(4)	μC,P 98.8(3,4.6) μC,Pt 49.7(2,0) μC,Ru 50.6(2,6) Ru,Pt 61.04(3,13)	[46]
				RuC_4PPt_2	OC 1.894(10,6) μOC 2.139(10,20) P 2.427(3)		Pt,Pt 57.92(4)	
$(Ph_3P)_2(\mu\text{-CO})Pt_2$. $(\mu\text{-}CO)_2Os(CO)_2$. (PPh_3)	tr P$\bar{1}$ 2	13.593(4) 15.839(4) 12.633(8)	102.97(3) 108.18(2) 84.86(3)	PtC_2POsPt	μOC 2.045(6,17) P 2.262(2,2)	Os 2.739(1,5) C not given Pt 2.650(1) C not given	not given	[47a]
				OsC_4PPt_2	Cl 2.247(11) μOC 2.124(7,4) P 2.423(2)		not given	
$[(PPh_3)_2(\mu\text{-}PPh_2)Pt_2$. $(\mu\text{-}CO)_3Mo(cp)]$. H_2O (at 173 K)	tr P$\bar{1}$ 2	12.053(1) 13.690(1) 17.292(3)	109.271(6) 92.541(6) 106.169(6)	PtC_2P_2MoPt	μOC not given μP 2.283(2,1) Ph_3P 2.258(2,4)	Mo 2.805(-,9) Pt 2.6048(3) P 69.55(4)	Mo,Pt 62.33(1,35)	[47b]
				MoC_8Pt_2	μOC not given cpC not given		Pt,Pt 55.33(1)	

Continued **Table 2.** Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Á] b [Á] c [Á]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Á]	M - M [Á] M – L - M [°]	L – M - L [°]	Ref
$(NBu_4)[(C_6F_5)_4.(\mu\text{-}C_6F_5)_2Pt_2Ag.(OEt_2)].C_6H_{14}$ (yellow)	m $P2_1/c$ 4	11.278(6) 25.643(8) 22.359(7)	 94.92(3) 	PtC_4AgPt $AgOPt_2$	C 2.03(2,4) μC 2.23(2,5) O 2.259(1)	Ag 2.809(2,6) Pt 2.687(1) C 73.9(6,2)	μC,μC 101.1(6,1) μC,Ag 83.9(5,1.4) C,Ag 103.0(5,3.0) μC,Pt 53.0(5,1.5) C,Pt 135.3(5,2.6) Ag,Pt 61.43(4,2.2) O,Pt 150.77(7,15) Pt,Pt 57.13(3)	[48]
$(NBu_4)[(C_6F_5)_4.(\mu\text{-}C_6F_5)_2Pt_2Ag.(tht)].0.5C_6H_{14}$ ((yellow)	m $P2_1/c$ 4	11.112(1) 25.671(2) 22.803(2)	 93.27(1) 	PtC_4AgPt $AgSPt_2$	C 2.033(8,11) μC 2.200(9,17) 2.277(9,17) thtS 2.421(3)	Ag 2.811(1,13) Pt 2.702(1) C 74.2(3,7)	C,C 87.5(3,4) μC,μC 100.4(3,0) μC,Ag 84.1(3,9) C,Ag 102.3(3,2.3) S,Pt 151.2(1,4.2) Pt,Pt 57.4(1)	[49]
$(NBu_4)[(C_6(\mu\text{-}F_5)_4.(\mu\text{-}C_6F_5)_2Pt_2Ag.(OEt_2)].Et_2O$ (yellow)	m $P2_1/c$ 4	11.278(6) 25.643(8) 22.359(7)	 94.92(3) 	PtC_4AgPt $AgOPt_2$	C 2.04(2,2) μC 2.24(2,5) O not given	Ag 2.821(2,6) Pt 2.698(1) C 74.1	not given not given	[50]
$(Ph_3P)_3(OC)Pt_2.(\mu_3\text{-}S)CuCl$	m $P2_1/n$ 4	11.932(1) 30.210(2) 13.946(1)	 91.36(1) 	PtP_2SCuPt PtCSPCuPt $CuClSPt_2$	Ph_3P 2.269(2,7) μ_3S 2.288(2) OC 1.842(9) μ_3S 2.285(2) Ph_3P 2.316(2) Cl 2.172(2) μ_3S 2.210(2)	Cu 2.821(1,67) S 78.0(1,1.9) Pt 2.657(1) S 71.0(1)	P,P 102.2(1) μ_3S,Pt 54.4(1) μ_3S,Cu 50.7(1) Cu,Pt 64.2(1) C,P 97.9(3) μ_3S,Pt 54.5(1) μ_3S,Cu 48.9(1) Cu,Pt 59.9(1) Cl,μ_3S 175.1(1) μ_3S,Pt 51.0(1,3) Pt,Pt 55.9(1)	[51]
$[(Ph_3P)_2(\mu\text{-}CO)Pt_2.(\mu\text{-}I)_2Os(CO)_2.(PPh_3)].0.5C_6H_{14}$ (yellow orange)	m $P2_1/c$ 4	21.073(4) 15.533(3) 18.753(3)	 109.86(2) 	PtCPIOsPt $OsC_2I_2PPt_2$	μOC 1.96(3,2) Ph_3P 2.249(8,1) μI 2.719(2,26) OC 1.81(4,6) μI 2.778(2,9) Ph_3P 2.380(8)	Os 2.824(2,28) I not given Pt 2.685(2) C not given	not given not given	[52]
$(Ph_3P)_2(\mu\text{-}CO)Pt_2.(\mu\text{-}\eta^2\text{:}\eta^6\text{-dmdb}).Mo(CO)_3$ (red)	m $P2_1/n$ 4	13.047(2) 13.856(2) 27.103(6)	 102.13(2) 	PtCPMoPt PtHCBPMoPt $MoC_4B_4Pt_2$	μOC 2.026(7) Ph_3P 2.275(2) H 1.773 μOC 1.996(8) μB 2.359(9) Ph_3P 2.268(2) OC 2.035(8,21) $\mu\eta^6$C 2.270(7) B 2.417(8,49) μB 2.325(9)	Mo 2.707(1) 2.950(1) P t 2.747(1) C 86.2(3) B 65.5(1)	P,Pt 143.8(1) P,Mo 149.1(1) Mo,Pt 65.5(1) P,Pt 136.4(1) P,Mo 166.7(1) Mo,Pt 56.6(1) Pt,Pt 57.9(1)	[53]
$(MeBu^t_2P)_2(OC)_2.\{\mu\text{-}C(OMe)Ph\}.W(CO)_4$ (red)	m $P2_1/a$ 4	16.003(5) 15.691(7) 15.261(9)	 93.52(4) 	PtC_2PWPt WC_4Pt_2	μOC 1.87(4,1) μC 2.06(2,2) P 2.349(7,1) OC 1.92(3,1) 2.03(3,3)	W 2.830(2,2) Pt 2.627(1) C 79.5(8)	μC,Pt 50.2(7,5) P,Pt 149.1(2,2) W,Pt 62.3(2,1) C,C 87(1,3) 173(1) Pt,Pt 55.3(2)	[54]
B: Pt-M BONDS (Pt-Pt NOT)								
$(Ph_2pyP)_2(OC)_2.Pt_2(\mu_3\text{-}Se)Fe(CO)_3$ (yellow orange)	m $P2_1/n$ 4	10.831(4) 17.256(5) 21.385(3)	 101.89(5) 	PtCPSeFe FeC_3SePt_2	OC 1.856(6,4) P 2.303(1,1) OC 1.768(6,18) μ_3Se 2.3371(11)	Fe 2.5482(10) 2.5773(8) Se 65.19(4,64) Pt 3.167(9) Se 81.81(2)	C,P 99.7(1,2) C,μ_3Se 153.7(1,1.9) P,μ_3Se 106.2(1,2.2) C,Fe 98.0(1,1.9) P,Fe 160.89(4,3.35) μ_3Se,Fe 55.87(3,4) C,C 99.4(3,2.3) C,μ_3S 103.4(1,4) 144.88(17) μ_3S,Pt 58.93(4,59) Pt,Pt 76.32(3)	[55a]

Continued **Table 2.** Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$-Se)$Fe(CO)_3$ (dark yellow)	tr P$\bar{1}$ 2	10.598(2) 10.880(3) 18.824(1)	75.17(1) 80.87(1) 73.72(2)	PtCPSeFe FeC_3SePt_2	OC 1.847(8,2) Ph_3P 2.307(2,5) μ_3Se 2.418(1,4) OC 1.768(9,3) μ_3Se 2.343(1)	Fe 2.560(1,3) Se 65.04(3,14) Pt 3.178(1) Se 82.14(3)	C,P 100.9(2,2.6) C,μ_3Se152.9(2,1.2) P,μ_3Se106.0(1,1.5) Fe,Pt 51.64(2,8) C,C 98.7(4,1.9) C,μ_3S 103.4(3,3.3)	[55b]
$[(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$-η^1:η^1-PhC≡CPh). $Fe(CO)_3]C_6H_{14}$ (red)	or Pbca 8	21.407(2) 19.973(7) 24.029(4)		PtC_2PFe FeC_5Pt_2	OC not given μC 2.10(2,1) P 2.322(6,4) OC not given μC 2.14(2,0)	Fe 2.531(3) 2.608(3) Pt 3.013(1)	Fe,Pt 54.10(7,1.2) Pt,Pt 71.79(8)	[56]
$[(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$-η^1:η^1-PhC≡C. C≡CPh)Fe$(CO)_3]$ $CHCl_3$ (red)	m $P2_1/c$ 4	13.152(5) 23.707(13) 18.407(10)	103.31(4)	PtC_2PFe FeC_5Pt	OC 1.91(2,2) μC 2.078(14,13) P 2.336(4,1) OC not given μC 2.149(14,51)	Fe 2.596(2,2) Pt 3.072(1)	not given not given	[57]
$[(mesNC)_2Pt_2.$ $(\mu$-η^3-dpmp$)_2.$ Pd$](PF_6)_2$ (at 126 K)	m C2/c 4	22.209(6) 23.777(4) 20.136(3)	117.44(3)	PtP_2CPd PdP_2Pt_2	$\mu\eta^3$P 2.274(8) 2.323(8) C 1.97(2) $\mu\eta^3$P 2.298(8,0)	Pd 2.599(3,0) Pt 3.290(3)	P,P 161.3(3) P,C 99.1(9,4) P,Pd 80.8(2,4.8) C,Pd 173.3(8) P,P 115.4(4) P,Pt 84.0(2) 158.7(2) Pt,Pt 78.5(1)	[58]
$[(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$-η^1:η^1-PhC≡C. C≡CPh)Fe$(CO)_3]$. C_6H_6 (red)	tr P$\bar{1}$ 2	13.564(9) 13.914(12) 15.410(2)	79.29(7) 86.51(7) 86.45(6)	PtC_2PFe FeC_5Pt_2	OC 1.90(2,0) μC 2.085(12,12) P 2.337(4,8) OC not given μC 2.118(12,21)	Fe 2.608(3,2) Pt 2.939(2)	not given not given	[57]
$[(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$ –η^1:η^1-PhC≡CPh). $Os(CO)_3]C_6H_{14}$ (red)	or Pbca 8	21.408(3) 19.848(3) 24.135(5)		PtC_2POs OsC_5Pt_2	OC not given μC 2.09(2,0) P 2.316(5) OC not given μC 2.27(2,2)	Os 2.647(2) 2.688(2) Pt 3.080(1)	Os,Pt 54.7(1,6) Pt,Pt 70.71(8)	[56]
$[(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3$-MeC≡CMe). $Os(CO)_3$ (yellow) (at 200 K)	m $P2_1/c$ 4	11.143(8) 17.458(12) 23.443(15)	113.82(5)	PtC_2POs OsC_5Pt_2	OC 1.87(1,1) μC 2.058(8,3) P 2.305(4,5) OC 1.89(1,1) μC 2.22(1,1)	Os 2.664(2) 2.669(2) Pt 3.033(2)	C,P 100.2(4,2.3) C,Os 102.3(4,1.6) Os,Pt 55.33(4,9) C,Pt 95(4,75 Pt,Pt 69.33(3)	[59]
$[(Ph_3P)_2(OC)_2.Pt_2.$ $(\mu_3$-η^1:η^1-PhC≡C. C≡CPh)Ru$(CO)_3]$. C_6H_6 (red)	tr P$\bar{1}$ 2	13.581(12) 14.048(10) 15.346(9)	79.32(5) 85.49(6) 85.88(6)	PtC_2PRu RuC_5Pt_2	OC 1.87(2,2) μC 2.06(2,1) P 2.337(5,10) OC not given μC 2.24(2,5)	Ru 2.697(2,2) Pt 2.9595(13)	not given not given	[57]
$(NBu_4)[(C_6F_5)_2(\mu$-Cl$)_2.$ $Pt_2Ag(OEt_2)]$ (pale yellow)	m $P2_1/n$ 4	12.574(2) 14.749(2) 27.983(3)	92.73(1)	PtC_2Cl_2Ag $AgOPt_2$	C 1.969(15,18) μCl 2.406(3,8) O 2.298(10)	Ag 2.759(1) 2.782(1) Pt 3.263(1)	C,C 89.1(5,2.1) Cl,Cl 84.4(1,1) C,Cl 93.3(4,1.2) 177.4(4,1.3) C,Ag 98.7(4,6.1) Cl,Ag 80.7(1,5.3) O,Pt 139.6(3,4.1) Pt,Pt 72.15(3)	[60]
$(MePh_2P)_2(OC)_2Pt_2.$ $(\mu_3$-CC_6H_4Me-4). W$(CO)_2(\eta^5$-cp)	m $P2_1/c$ 4	14.932(13) 11.438(11) 26.394(24)	97.42(7)	PtC_2PW WC_6Pt_2	OC 1.83(5) μ_3C 2.05(4,1) P 2.313(12) 2.337(12) OC 1.89(5,5) μ_3C 2.04(4) η^5cpC not given	W 2.785(3,0) C 76(2,6) Pt 2.989(3) C 93.2(15)	C,P 97(1,3) C,W 111.8(14) 141.9(14) P,W 136.0(3,11.9) W,Pt 57.6(1,1) Pt,Pt 64.9(1)	[61]

Continued Table 2. Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Á] b [Á] c [Á]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Á]	M - M [Á] M – L - M [°]	L – M - L [°]	Ref
$(Ph_3P)_2(OC)_2Pt_2.$ $(\mu_3\text{-As})Mo(CO)_2.$ $(\eta^5\text{-cp})$ (red brown)	tr P$\bar{1}$ 2	11.66(1) 12.15(1) 17.19(1)	76.99(6) 74.89(6) 83.98(6)	PtC_2P_2AsMo	OC 1.810(42,8) P 2.287(9,1) μ_3As 2.425(3,4)	Mo 2.777(3) 2.799(3) As 67.2(1,4) Pt 3.055(1) As 78.1(1)	C,P 101.0(14,1.0) C,As 158.5(15,1.4) C,Mo 99.3(15,1.5) P,As 100.4(2,2.5) P,Mo 155.4(2,4.6) As,Mo 59.5(1,1) Mo,Pt 56.7(1,4)	[62]
				MoC_7AsPt_2	OC 1.935(29,4) η^5cpC not given μ_3As 2.606(4)		C,C 90.2(11) C,As 72.4(10,1.3) C,Pt 78.8(9,1.0) 125.5(10,1.4) As,Pt 53.3(1,2) Pt,Pt 66.4(1)	
$[(C_6F_5)_4(\mu\text{-OH}).$ $(\mu\text{-}\eta^2\text{-dppm})Pt_2.$ $Ag(PPh_3)]$tol (yellow)	m $P2_1/n$ 4	14.360(1) 21.590(1) 21.585(2)	90.85(1)	PtC_2OPAg	C 2.004(12,12) 2.065(11,7) μO 2.092(7,8) $\mu\eta^2$P 2.299(3,3)	Ag 2.791(1) 2.833(1) Pt 3.479(1) O 112.5(3)	C,C 90.5(4,10) O,P 88.4(2,1)	[63]
				$AgPPt_2$	Ph_3P 2.422(3)		P,Pt 141.8(1,1.3) Pt,Pt 76.4(1)	
C: Pt-Pt BOND								
$(Ph_3P)_3(OC)Pt_2.$ $(\mu_3\text{-S})AgCl$ (yellow)	m $P2_1/n$ 4	12.010(2) 30.195(6) 13.897(3)	91.62(3)	PtP_2SPt	P 2.267(2,9) μ_3S 2.278(2)	Ag 2.965(1,59) S 78.1(1,1.8) Pt 2.658(1) S 71.4(1)	P,P 102.2(1) P,Pt 103.4(1) 154.3(1) μ_3S,Pt 54.3(1)	[51]
				PtCSPPt	OC 1.856(10) μ_3S 2.279(2) P 2.332(2)		C,Pt 105.0(2) μ_3S,Pt 54.1) P,Pt 157.0(1) Ag,Pt 61.1(1)	
				AgClS	Cl 2.352(3) μ_3S 2.427(3)		Cl,μ_3S 171.5(1) Pt,Pt 51.2(1)	
$[(\mu\text{-}\eta^2\text{-dppm})Pt_2.$ $(\mu_3\text{-S})(\mu\text{-}\eta^2\text{-dppm})_2.$ $Au]Cl.Me_2CO$ (yellow)	tr P$\bar{1}$ 2	11.913(2) 27.870(6) 11.158(2)	92.01(1) 95.21(1) 88.87(2)	PtP_2SPt	$\mu\eta^2$P 2.256(9,19) μ_3S 2.296(8,5)	Au 3.113(2) 3.259(2) S 80.5(3,2.4) Pt 2.615(2) S 69.4(2)	P,P 106.6(3,3.4) P,μ_3S 101.9(3,1.3) P,Pt 95.0(3,7) 155.7(2,1.2) μ_3S,Pt 55.3(2,2) Au,Pt 65.79(5,2.8)	[64]
				AuP_2S	$\mu\eta^2$P 2.340(9,14) μ_3S 2.621(8)		P,P 143.9(3) P,μ_3S 107.5(3,5.8) Pt,Pt 48.41(4)	
$[(Ph_3P)_3(OC)Pt_2.$ $(\mu_3\text{-S})Au(PPh_3)].$ $PF_6.CH_2Cl_2$ (orange)	tr P$\bar{1}$ 2	11.065(22) 13.903(13) 26.439(13)	89.81(6) 79.31(8) 79.00(12)	PtCPSPt	OC 1.87(5) P 2.34(1) μ_3S2.302(9)	Au 3.016(2) S 81.3(3) Pt 2.649(2) S 76.3(2)	C,P 94.9(14) μ_3S,P 105.5(3) P,Pt 159.2(2) μ_3S,Pt 54.9(2)	[65]
				Pt P_2SPt	P 2.281,1) μ_3S 2.301(8)	Au 3.312(2) S 91.3(3)	P,P 1039(4) P,μ_3S 101.8(3) 153.8(4) P,Pt 100.1(3 155.4(3)) μ_3S,Pt 54.9(2)	
				AuPS	P 2.28(1) μ_3S 2.329(9)		P,μ_3S 177.3(4)	
D: SUILFIDE-BICAPPED MPt_2 TRIANGLE								
$[(Ph_3P)_4Pt_2.$ $(\mu_3\text{-S})_2Cu(PPh_3)].$ PF_6 (orange)	or $P2_12_12_1$ 4	14.261(3) 18.878(5) 29.831(8)		$Pt^{II}S_2P_2$	μ_3S 2.356(5,14) P 2.286(5,1) 2.305(5,0)	Cu 2.869(2,9) S 76.1(2,5) Pt not given S 89.7(2)	μ_3S,μ_3S81.5(2,1) P,P 101.0(2,9) μ_3S,P 88.7(2,2.4) 169.8(2,3.2)	[66]
				Cu^IS_2P	μ_3S 2.286(5,17) P 2.174(5)		μ_3S,μ_3S 2 84.6(2) μ_3S,P 137.5(4,1.9)	
$[(Ph_3P)_4Pt_2(\mu_3\text{-S})_2.$ $Rh(CO)_2]Me_2CO$ (brown)	m $P2_1/c$ 4	16.813(3) 16.068(4) 28.342(5)	99.24(2)	$Pt^{II}S_2P_2$	μ_3S 2.352(3,16) P 2.281(3,8)	Rh 3.041(1,7) S 80.5(1,5) Pt 3.269(1) S 88.0(1,1)	P,P 99.6(1,7) P,μ_3S 90.2(1,2.6) 170.0(1,3.0)	[67]
				$Rh^IC_2S_2$	OC 1.844(14,12) μ_3S 2.355(3,2)		C,C 99.6(6) μ_3S,μ_3S 79.9(1) C,μ_3S 92.4(4,6) 172.1(4,8)	
				$Rh^IC_2Cl_2$ (monomer)	OC 1.861(18,28) Cl 2.339(6,12)		C,C 91.0(8) Cl,Cl 89.7(2)	

Continued **Table 2.** Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Rh.(\eta^4\text{-cod})]PF_6CH_2Cl_2$ (yellow)	m $P2_1/c$ 4	16.681(2) 17.181(5) 27.476(2)	 103.58(4) 	$Pt^{II}S_2P_2$ $Rh^{I}C_4S_2$	μ_3S 2.347(3,12) P 2.280(3,9) η^4C 2.155(16,12) μ_3S 2.346(3,3)	Rh 3.051(1,11) S 81.1(1,6) Pt 3.255(1) S 87.7(1,2)	P,P 98.7(1,4) P,μ_3S 90.9(1,1.9) 169.7(1,1.2) μ_3S,μ_3S 79.6(1)	[68]
$(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Rh.(dmpNC)_2]PF_6$ (yellow)	m C2/c 4	22.089(8) 18.141(7) 21.363(11)	 105.35(4) 	$Pt^{II}S_2P_2$ $Rh^{I}C_2S_2$	μ_3S 2.351(2,18) P 2.278(2,10) C 1.90(1,0) μ_3S 2.365(2,0)	Rh 3.054(1,0) S 80.7(1,4) Pt 3.2907(6) S 88.8(1)	μ_3S,μ_3S 79.5(1) P,P 98.5(1) μ_3S,P 90.9(1,2.4) 169.7(1,1.7) C,C 94.2(6) μ_3S,μ_3S 79.0(1)	[67]
$(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Ag(PPh_3)]PF_6$ (orange)	or $P2_12_12_1$ 4	14.229(1) 18.674(1) 30.127(1)	 	$Pt^{II}S_2P_2$ $Ag^{I}S_2P$	μ_3S 2.359(1,12) P 2.284(1,1) 2.301(1,7) μ_3S 2.479(1) 2.585(1) P 2.327(1)	Ag 3.036(1,3) S 77.47(3,1.33) Pt 3.351(2) S 90.50(3,1)	μ_3S,μ_3S 82.80(3,10) P,P 101.18(3,1.25) μ_3S,P 88.10(3,1.46) 170.78(3,1.25) μ_3S,μ_3S 76.04(3) μ_3S,P 141.66(3,5.13)	[51]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Ag(PPh_3)]PF_6$ (orange)	tr $P\bar{1}$ 2	14.934(1) 15.039(1) 19.744(1)	74.55(1) 88.01(1) 79.88(1)	$Pt^{II}S_2P_2$ $Ag^{I}S_2P$	μ_3S 2.358(2,15) P 2.288(2,10) μ_3S 2.502(2) 2.607(2) P 2.343(2)	Ag 2.962(1) 3.240(1) S 78.3(1,5.3) Pt 3.375(2) S 91.37(7,12)	μ_3S,μ_3S 81.76(7,39) P,P 3.69(8,3.06) μ_3S,P 87.42(7,1.44) 168.26(7,58) μ_3S,μ_3S 74.33(7) μ_3S,P 42.82(8,7.36)	[51]
$(Ph_3P)_4Pt_2\text{-}(\mu_3\text{-}S)_2CoCl_2$ (yellow green)	m C2/c 4	20.176(7) 18.956(7) 17.517(5)	 92.97(3) 	$Pt^{II}S_2P_2$ $Co^{II}Cl_2S_2$	μ_3S 2.348(4,8) P 2.288(4,21) Cl 2.232(6) μ_3S 2.359(4)	Co 3.066(1,0) S 85.8(1) Pt not given	μ_3S,μ_3S 80.5(1) P,P 99.0(1) μ_3S,P 90.3(1,2.3) 170.5(1,2.0) Cl,Cl 104.8(2) μ_3S,μ_3S 80.0(2) Cl,μ_3S 117.9(1,2.4)	[69]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Rh(CO)(PPh_3)].PF_6\cdot CH_2Cl_2$ (yellow)	or Pbca 8	24.401(8) 25.817(6) 27.675(4)	 	$Pt^{II}S_2P_2$ $Rh^{I}S_2CP$	μ_3S 2.352(1,22) P 2.285(1,11) μ_3S 2.375(1,13) OC 1.867(7) P 2.261(2)	Rh 3.078(1,12) S 81.26(4,1.1) Pt 3.312(5) S 89.49(4,5)	μ_3S,μ_3S 78.84(4,4) P,P 99.41(5,59) μ_3S,P 92.78(5,4.34) 168.99(5,4.4) μ_3S,μ_3S 77.94(5) μ_3S,C 91.8(2) 169.0(2) μ_3S,P 99.41(5) 174.33(5) C,P 91.1(2)	[70]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Re(CO)_3].[Re_3(OMe)_4(CO)_9]$	m $P2_1/c$ 4	19.05(2) 18.187(3) 28.34(1)	 96.93(3) 	$Pt^{II}S_2P_2$ ReC_3S_2	μ_3S 2.36(2,5) P not given OC not given μ_3S 2.40(2,0)	Re 3.083(6,16) Pt 3.275(5)	not given not given	[71]
$[(Ph_3P)_4Pt_2\text{-}(\mu_3\text{-}S)_2Ir(CO)(PPh_3)].PF_6\cdot 0.5CH_2Cl_2$ (dark yellow)	or Pbca 8	24.42(5) 25.879(2) 27.683(2)	 	$Pt^{II}S_2P_2$ $Ir^{I}S_2CP$	μ_3S 2.355(2,17) Ph_3 2.287(2,9) μ_3S 2.375(2,12) OC not given Ph_3P not given	Ir 3.092(-,10) S 81.64(5,1.2) Pt 3.315(5) S 89.20(6,61)	S,S 78.66(6,2) P,P 99.41(7,53) S,P 90.96(6,4.68) 168.81(6,4.31) μ_3S,S 78.10(6) S,C 92.7(2) 170.2(2) S,P 98.92(6) 174.53(8)	[70]
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2\text{-}Re(CO)_3]BF_4$ (red)	m $P2_1/n$ 4	17.054(4) 23.826(4) 18.452(4)	 102.33(2) 	$Pt^{II}S_2P_2$ $Re^{I}C_3S_2$	μ_3S 2.366(4,18) P not given OC 1.862(1,33) μ_3S 2.454(3,3)	Re 3.0668(9) 3.1678(8) S not given Pt 3.255 S 86.9(1,2)	μ_3S,μ_3S 81.2(1,1) C,C 85.2(7,1.2) μ_3S,μ_3S 78.1(1)	[71]

Continued **Table 2.** Crystallographic and structural data for Pt_2M triangular compounds, (M = transition metal, uranium)[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Á] b [Á] c [Á]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Á]	M - M [Á] M – L - M [°]	L – M - L [°]	Ref
$(Ph_3P)_4Pt_{1.9}(\mu_3\text{-}S)_2$. $Pd_{1.1}(Cl)(PPh_3)]$. $PF_6.H_2O$ (orange)	or Pbca 8	24.046(3) 25.411(3) 27.300(3)		$M^{II}S_2P_2$ (x2)	μ_3S 2.358(1,27) P 2.293(1,8)	M 3.100(2,33) 3.294(2) S 84.74(4,3.5)	μ_3S,μ_3S 77.56(4,10) P,P 99.23(5,22) μ_3S,P 91.58(5,4.5) 167.71(5,5.0)	[70]
				$M^{II}S_2ClP$	μ_3S 2.318(1,0) P 2.270(1) Cl 2.369(1)		μ_3S,μ_3S 78.39(4) Cl,P 91.94(5) S,P 99.77(5) 177.26(5) S,Cl 90.89(5) 166.49(5)	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Au(\eta^2\text{-pap})]BF_4$. $4.5CH_2Cl_2$ (orange) (at 223(2) K)	m $P2_1/c$ 4	26.6932(4) 15.063(2) 26.8548(4)	105.519(1)	$Pt^{II}S_2P_2$	μ_3S 2.360(4,18) P 2.291(5,6)	Au 3.099 3.196 S 83.3(1,2.2) Pt 3.268 S 87.6(1,3)	μ_3S,μ_3S 77.9(1,2) P,P 99.2(1,4) μ_3S,P 91.7(1,2.0) 169.0(1,1.2)	[28]
				$Au^{III}S_2NC$	μ_3S 2.376(4,10) η^2N 2.075(15) C 2.039(17)		μ_3S,μ_3S 77.28(14) N,C 89.6(7)[c]	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Au(\eta^2\text{-topy})]BF_4$[d] (orange)	tr $P\bar{1}$ 2	18.0900(2) 21.3643(2) 23.0658(2)	98.643(1) 95.966(1) 93.923(1)	$Pt^{II}S_2P_2$	μ_3S 2.367(3,10) P 2.271(3,3) 2.299(3,3)	Au not given S 82.6(1,2) Pt not given S 87.9(1,4)	μ_3S,μ_3S78.1(1,1) P,P 99.4(1,5) μ_3S,P167.06(12)	[72]
				$Au^{III}S_2NC$	μ_3S 2.364(4,7) η^2N 2.18(2) C 1.94(3)		μ_3S,μ_3S 78.31(11) N,C81.0(9)[e]	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $VO(OMe)_2]PF_6$ (red)	m $C2_1/n$ 8	17.7574(4) 41.8464(9) 19.3758(4)	92.614(1)	$Pt^{II}S_2P_2$	μ_3S 2.347(4,10) P 2.286(4,9) 2.304(4,3)	V 3.204(3,16) S 83.4(1,6) Pt 3.317(2) S 89.9(1,2)	μ_3S,μ_3S 77.9(1,1)	[73]
				$V^{V}O_3S_2$	O 1.618(13) MeO1.783(15,35) μ_3S 2.466(5,10)		μ_3S,μ_3S 73.47(14)	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $UO_2(\eta^2\text{-}O_2NO)_2]$ (purple)	m $P2_1/c$ 4	22.5463(9) 14.2378(6) 23.8747(10)	115.291(1)	$Pt^{II}S_2P_2$	μ_3S 2.334(1,1) 2.339(1,1) P 2.278(1,6) 2.308(1,5)	U 3.5589(4) 3.6368(4) S 86.7(-,1.2) Pt 3.2842(17) S 89.7(-,1)	μ_3S,μ_3S 78.79(5,5) P,P 99.86(6,8)	[73]
				$U^{VI}O_6S_2$	O 1.693(4,49) η^2O 2.505(5,8) μ_3S 2.873(1,4)		not given	
$[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2$. $Au(PPh_3)]NO_3$ $0.5H_2O$ (yellow)	tr $P\bar{1}$ 2	14.605(1) 15.989(2) 18.005(2)	101.144(8) 100.773(7) 91.201(2)	$Pt^{II}S_2P_2$	μ_3S 2.353(2,24) P 2.283(2,16)	Au 3.231(1) 3.314(1) S 81.6(1,7.6) Pt 3.279(1) S 88.3(1,7)	μ_3S,μ_3S 82.4(1,0) P,P 98.9(1,4) μ_3S,P 89.4(1,3.0) 171.3(1,3.3)	[74]
				$Au^{I}S_2P$	μ_3S 2.345(2) 2.959(2) P 2.243(2)		S,P 120.8(1)	
$[(Ph_3P)_4(\mu\text{-}S)Pt_2$. $(\mu_3\text{-}S)Au(PPh_3)]$. PF_6. (yellow)	tr $P\bar{1}$ 2	15.0340(5) 15.5009(5) 21.9604(7)	74.805(1) 85.733(1) 78.553(1)	$Pt^{II}S_2P_2$	μS 2.346(2,10) μ_3S 2.369(2,10) P 2.299(2,16)	Au 3.103(1) 3.465(5) S 89.2(-,6.9) Pt 3.390(5)	$\mu S,\mu_3S$ 81.41(7,41) P,P 103.21(9,2.65) S,P 87.7(-,4.0) 168.8(-,4.5) μ_3S,P 172.14(8)	[75]
				$Au^{I}SP$	μ_3S 2.338(2) P 2.252(2)			

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. Six-membered metallocyclic ring.
d. There are two crystallographically independent molecules.
e. Five-membered metallocyclic ring.

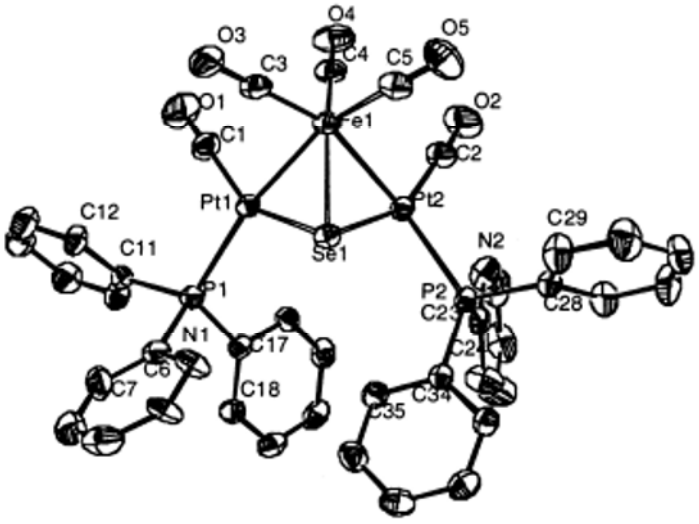

Figure 3. Structure of $(Ph_2pyP)_2(OC)_2Pt_2(\mu_3\text{-}S)Fe(CO)_3$ [55a].

complex [38]. Both Pt-Fe bond distances are equal to 2.541(3) Å and the Pt-Pt bond distance is 2.581(1) Å. The Pt-Fe-Pt' angle of 61.09(9)º is only about 1.6º greater than the Pt-Pt'-Fe angles with the values of 59.47(8) and 59.48(7)º, respectively. The Pt-Pt bond distances range from 2.581(1) Å [38] to 2.837(1) Å [43] with a mean value of 2.682 Å. The Pt-M-Pt angles range from 57.7 to 64.2º and Pt-Pt-M from 54.4 to 64.6º. Interestingly, the mean values are almost equal, with values of 59.9 and 60.1º, respectively. Noticeably, the mean values of the sum of all three metal-metal bond distances increase with the covalent radius of M: 7.71 Å (Fe, 1.20 Å) < 7.97 Å (Co/Ru 1.26 Å) < 8.04 Å (Cu, 1.38 Å) < 8.13 Å (Au, 1.43 Å) < 8.16 Å (Mo, 1.45 Å) < 8.28 Å (W, 1.46 Å) < 8.32 Å (Ag, 1.53 Å). However, there is an exception for 8.23 Å (Os, 1.28 Å). For this we have no explanation.

2.2.1.2. Pt-M bonds, no Pt-Pt bonds

There are fourteen examples of Pt_2M triangular geometry with a Pt...Pt open edge. Their crystallographic and structural data are given in Table 2B. Structures are listed in order of the elongated sum of two Pt-M bond lengths.

The two yellow orange Pt_2Fe [55] and red brown Pt_2Mo [62] complexes contain an inner MPt_2X skeleton (M=Fe and X=Se, or M=Mo and X=As). The structure of one of these complexes is shown in Fig. 3. The $FePt_2Se$ inner skeleton may be described as a butterfly with two FePtSe triangles hinged at the Fe-Se vector, the dihedral angle being 87.68(2)º. The two platinum atoms are non bonded, and the Pt(1)-Pt(2) distance is 3.167(9) Å. By considering the two Pt-Fe bonds (av. 2.563 Å), the coordination sphere of iron is roughly octahedral, the three Fe-CO bonds being staggered with respect to the Fe-Se bond as well as to the two Fe-Pt bonds. The coordination around the platinum atoms is almost square-planar (PtCPSeFe). The structure of the Pt_2Mo derivative [62] is similar to the butterfly inner skeleton of $MoPt_2As$. The butterfly with the two MoPtAs triangles is hinged at the Mo-As vector. The mean Pt-Mo bond distance is 2.788 Å and the Pt...Pt separation is 3.055(1) Å. There is an interdependence between the M-M distance and the M-X-M bridge angle: as the former elongates, the latter opens. The Pt-M *vs.* Pt-X-M 2.563 Å *vs.* 65.2º (M=Fe, X=Se) and 2.788 Å *vs.* 67.2º (M=Mo, X=As) and Pt-Pt *vs.* Pt-X-M, 3.167(9) Å *vs.* 81.8(2) (X=Se and Fe) and 3.055(1) Å *vs.* 78.1(1)º (X=As and Mo), respectively.

The structures of another eight Pt_2M derivatives, Pt_2Fe [56,57], Pt_2Ru [57], Pt_2Os [56,59] and Pt_2W [61], consist of a triangular Pt_2M cluster with triply bridging carbon donor atom(s). The Pt-Pt distance ranges from 2.939(2) Å [57] to 3.080(1) Å [56] with a mean value of 3.019 Å. The mean Pt-M bond distance increases in the order: 2.591 Å (M=Fe) < 2.667 Å (Os) < 2.673 Å (Ru) < 2.785 Å (W).

The structure of $[(mesNC)_2Pt_2(\mu\text{-}\eta^2\text{-}dpmp)_2Pd]^{2+}$ [58] comprises an A-frame Pt_2Pd core bridged by two bis(diphenylphosphinomethyl)phenylphosphine (dpmp) ligands. The palladium atom occupies the central position between the two platinum atoms with equal Pd-Pt distances of 2.599(3) Å and a Pt-Pd-Pt angle of 78.5(1)º. The Pt...Pt separation of 3.290(3) Å is out of bonding range.

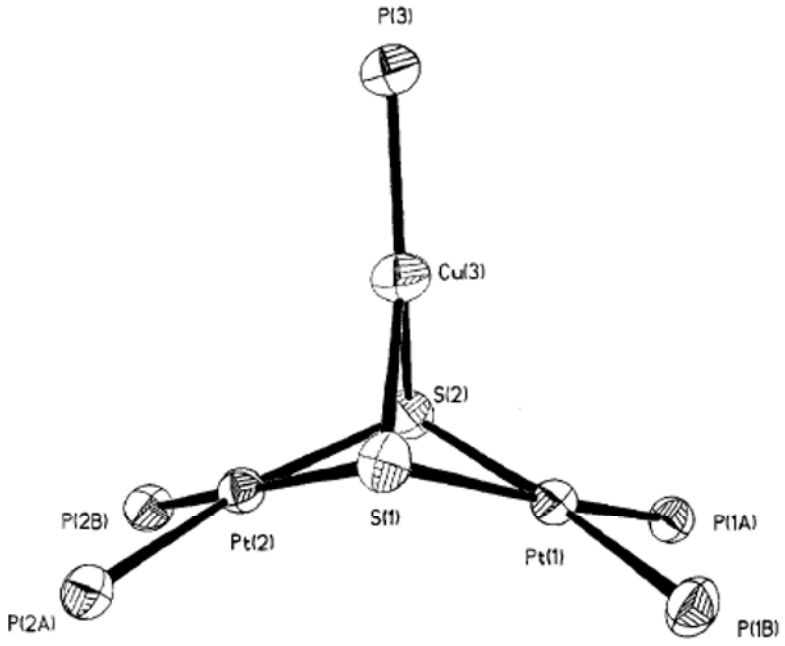

Figure 4. Structure of $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Cu(PPh_3)]^+$ [66] (phenyl groups are omitted for clarity).

In the pale yellow Pt_2Ag derivative [60], the core comprises two platinum atoms 3.263(1) Å apart, bridged by a single silver atom and two chlorine atoms. Each platinum center also has two terminal cis-C_6F_5 groups, which complete a distorted square pyramid (PtC_2Cl_2Ag). The two square pyramids share a pyramidal face, which is bounded by the two chlorine bridges and the silver atom. The two Pt-Ag distances differ slightly (Pt(1)-Ag(1) = 2.782(1) Å, Pt(2)-Ag(1) = 2.759(1) Å) with a Pt-Ag-Pt angle of 72.15(3)º. The silver atom is triply coordinated, surrounded by the two platinum atoms and one diethyl ether molecule.

In another yellow Pt_2Ag derivative [63], the core comprises two platinum atoms 3.479(1) Å apart, bridged by a single silver atom, one OH group and one μ-η^2-dppm ligand. Each platinum center also has two terminal cis-C_6F_5 groups, which complete a distorted square pyramid (PtC_2OCAg). The two Pt-Ag distances differ slightly, 2.791(1) and 2.833(1) Å, with the Pt-Ag-Pt angle of 76.4(1)º. The silver atom is triply coordinated ($AgPt_2P$).

2.2.1.3. Pt-Pt bond, no Pt-M bonds

There are three examples of complexes containing a Pt-Pt bond and no Pt-M bonds: one Pt_2Ag [51] and two Pt_2Au [64,65]. Their structural data are given in Table 2C. All three complexes contain $Pt_2M(\mu_3\text{-}S)$ groups. The three metal atoms define a distorted triangle with Pt-Pt distances of 2.658(1) Å [51], 2.615(2) Å [64] and 2.649(2) Å [65]. These clearly demonstrate that the metal-metal bond remains localized between the platinum atoms and only weak (or no) bonds are formed between the platinum and silver [51] or gold atoms [64,65]. The mean Pt-S-M bond angles of 81.6º are about 11.3º more open than the Pt-S-Pt angles70.3º.

2.2.1.4. Sulfide-bicapped MPt_2 triangle

There are eighteen examples of this group and their structural data are summarized in Table 2D. The structure of the $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Cu(PPh_3)]^+$ cation [66] is shown in Fig. 4, as an example. The structure shows an approximately equilateral triangular arrangement of the platinum and copper atoms capped by two μ_3-sulphido ligands. The cation is best viewed as a sulphide-bicapped heterometallic (Pt_2Cu) triangle in a trigonal bipyramidal framework. The unexpectedly short Cu-Pt distances (av. 2.869(4) Å, the shortest in this group) are associated with a more open $\{Pt_2S_2\}$ butterfly core (~137.5(5)º. Each platinum(II) atom has a square-planar geometry (PtS_2P_2) and each copper(I) atom has a Y-shaped geometry (CuS_2P). All remaining complexes have a similar structure. The P donor atoms to Pt(II) are only from PPh_3 molecules, which, along with two μ_3-S atoms, form a square-planar geometry about all Pt(II) atoms in this group. The mean Pt-μ_3S bond distance is 2.355º (range 2.33-2.41 Å) and the Pt-P(Ph_3) distance is 2.288 Å (range 2.264 – 2.312 Å). Both of the mean distances are about 0.010 Å shorter than those found in the series of Pt_2M (M=non-transition metal) with a similar structure (Table 1). The Pt-Pt distances range

from 3.255(1) Å [68] to 3.390(5) Å [75] (av. 3.302 Å). There are nine different heterometal transition metals. The mean Pt-M distance increases in the following order (the number of examples is given in parentheses): 2.869 Å (M=Cu (x1)) < 3.056 Å (Rh (x4)) < 3.066 Å (Co (x1)) < 3.082 Å (Ag (x2)) < 3.092 Å (Ir (x1)) < 3.100 Å (Re (x2)) ~ 3.100 Å (Pd (x1)) < 3.206 Å (V (x1)) < 3.235 Å (Au (x4)).

There is even an example with an actinide, the Pt_2U derivative [73] which belongs to this group. The corresponding data are also included in Table 2D. The mean Pt-U distance of 3.598 Å is the largest in the group.

While the mean S-Pt-S and S-M-S angles differ from each other only by 1.6º degrees (the former is 79.8º and the latter 78.2º), the mean Pt-S-Pt and Pt-S-M angles differ by 6.8º, with the former more open (av. 88.8º) than the latter (av. 82º). While the former is about 1.3º larger than that found in the series with non-transition M, the latter is about 1.5º smaller (Table 1). There is one example, $[(Ph_3P)_4Pt_2(\mu_3\text{-}S)_2Ag(PPh_3)]PF_6$ [51] which exists in two isomeric forms, orthorhombic and triclinic, which differ mostly by degree of distortion. These are examples of distortion isomerism [37].

2.2.1.5. Pt-M-Pt linear core

There are twenty five Pt_2M derivatives, which contain a linear (or almost linear) Pt-M-Pt array. Their structural parameters are summarized in Table 3A. The structures are listed in increasing order of the sum of the two Pt-M lengths.

Structures of eight coloured Pt_2M derivatives [76,77] consist of trinuclear $[\{(H_3N)_2Pt(\mu\text{-}\eta^2\text{-}NHCOR)_2\}_2M]^{n+}$ (M=Fe(III), Ni(II), Co(II), Mn(II), Cu(II)(x2), R=Bu^t [76], Ni(II) and Cu(II) R=Me [77]) cations with M located at the centre. The platinum atoms are linked to the central metal atom through their amidate ligands and also by Pt-M bonds. The coordination sphere of the Pt(II) atom is completed by two NH_3 and two amidate (N) ligands in cis position to each other (PtN_4M). The central heterometal atoms are coordinated by four oxygen atoms of the amidate ligands (MO_4Pt_2). The shortest Pt-M bond distances are those of Pt-Fe, 2.5566(15) and 2.5718(15) Å [76] in the series of linear Pt-M-Pt complexes. The Pt-M-Pt bond angles range from 175 to 180º.

Two red-orange Pt_2Cu derivatives [24] are isostructural, contain $[\{Me_2Pt(\mu\text{-}\eta^3\text{-}dppy)\}_2.Cu]^+$ cations and ClO_4^- anions. The 2,6-bis(diphenylphosphino) pyridine (dppy) ligands in these complex cations all adopt coordination mode D. The pair of cis-coordinated phosphorus atoms belonging to different dppy ligands are coplanar with the methyl groups and the platinum(II) atom. Each of the dppy ligands is coordinated through the N atom of the pyridine ring and create four five-membered bimetallocycles (PtPCNCu) sharing two axes, PtCuPt as well as NCuN. The mean Pt-Cu bond distances are 2.606 and 2.607 Å. Each Cu(I) atom is tetrahedrally coordinated (CuN_2Pt_2), while each Pt(II) atom is square-pyramidally coordinated (PtC_2P_2Cu). The Pt-Cu-Pt bond angles deviate from the linear 180º by 47.3 and 45.7º, respectively.

There are twelve coloured Pt_2M derivatives in which $[\{(H_3N)_2Pt(\mu\text{-}\eta^2\text{-}L\text{-}N,O)_2\}_2M]^{n+}$ cations are centrosymmetric with M sitting in the center, M=Cu(II) [80(x2), 84(x2), 91], Pd(III) [81,82(x2)], Pd(II) [82(x2)], Mn(II) [84] and Ag(I) [87]. Each of the respective pairs of $\mu\text{-}\eta^2$-ligands-N,O, pyo [78], meu [79,80,82,89], met [80,84,87] and meu+mec [82] are coordinated to the Pt(II) atom through N and through the exocyclic O atom to the M atom, in a head-to-head orientation. Each Pt(II) atom has a square-pyramidal arrangement, PtN_4M.

In the yellow Pt_2Ag derivative [81], a pair of $(C_6F_5)_2(\eta^2\text{-}acac)Pt$ units are connected by a single silver atom, with Pt-Ag bond distances of 2.668(1) and 2.681(1) Å, and a Pt-Ag-Pt angle of 177.2(1)º. Another Pt_2Ag derivative [85] contains two independent, seemingly different $[\{(C_6F_5)_3Pt(\mu\text{-}tht)\}_2Ag]^-$ anions. In each case, the silver atom is located on an inversion center so that there are two half-anions in the crystallographic asymmetric unit. Each $(C_6F_5)_3Pt(tht)$ fragment is connected to the silver center through Pt → Ag and S → Ag donor → acceptor bonds. The platinum silver vector makes two different angles with the perpendicular of the basal plane of the two anions, 24.5(2)º and 31.9(1)º. The mean Pt-Ag as well Pt-S-Ag bridge angles are rather different as well in the two anions, 2.783(1) Å and 65.4(1)º, and 2.862(1) Å and 72.3(1)º, respectively.

The complex cation $[\{(Et_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)\}_2Ag]^+$ [86], with two Pt-Ag bond distances of 2.790(1) and 2.791(1) Å and the Ag-H-Pt bridge angles of 106(4) and 109(5)º, is the only example in which hydrid bridges are involved in addition to metal-metal bonds. The Pt-Ag-Pt angle is 166.04(5)º. In the red Pt_2Ag derivative [88], the pair of $\{(\eta^2\text{-}dpae)(Me)ClPt\}$ planar molecules and an Ag(I) cation are entrapped between the chloride ligands in the almost linear $AgCl_2$ unit (Cl-Ag-Cl, 164.87(5)º). The resulting trinuclear supercation adopts an asymmetric overall conformation. The Pt-Ag bond distances are both 2.895(1) Å. However, the Pt-Cl-Ag bridge angles are different, with values of 74.64(3) and 113.34(5)º. This is reflected in the Pt-Ag-Pt angle of 145.11(5)º.

Inspection of the data in Table 3A shows that the most common ligands are NH_3 and N-donors of several hetero-ligands-N,O. The mean Pt-NH_3 bond distance of 2.05 Å (range 2.02 – 2.09 Å) is about 0.035 Å longer that the mean Pt-N (hetero-L) distance of 2.015 Å. There

Table 3. Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: Pt-M-Pt								
[{$(H_3N)_2Pt(\mu$-η^2-$NHCOBu^t)_2\}_2Fe$].$(ClO_4)_3$ (red)	or $P2_12_12_1$ 4	10.8505(15) 18.607(3) 22.350(3)		$Pt^{II}N_4Fe$ $Fe^{III}O_4Pt_2$	H_3N^b 2.062(9,17) $\mu\eta^2$N 1.996(10,3) 2.014(11,4) $\mu\eta^2$O 1.966(8,17) 2.029(8,4)	Fe 2.5566(15) 2.5718(15)	N,N^b 90.0(4,3.6) O,O 90.0(4,6.6) Pt,Pt 176.40(8)	[76]
[{$(H_3N)_2Pt(\mu$-η^2-$NHCOBu^t)_2\}_2Ni$].$(ClO_4)_2$ (light green)	tr $P\bar{1}$ 4	15.4742(10) 15.5319(11) 17.0866(12)	87.575(1) 83.976(2) 86.810(2)	$Pt^{II}N_4Ni$ $Ni^{II}O_4Pt_2$	H_3N 2.057(9,7) $\mu\eta^2$N 2.018(9,9) $\mu\eta^2$O 2.007(7,2)	Ni2.5870(4,0)	N,N 90,0(4,2.2) O,O 90.0(3,1.0) Pt,Pt 180.0	[76]
[{$((Me)_2Pt(\mu$-η^3-$dppy)\}_2Cu$].ClO_4.$0.5H_2O$ (red orange)	tr $P\bar{1}$ 2	11.244(1) 13.793(2) 20.030(2)	96.824(2) 102.047(2) 111.745(2)	$Pt^{II}C_2P_2Cu$ $Cu^IN_2Pt_2$	MeC 2.08(1,3) $\mu\eta^3$P 2.299(3,2) 2.322(2,4) $\mu\eta^3$N 1.978(8,4)	Cu 2.591(1) 2.622(1)	C,C 83.2(4,7) P,P 99.1(1,2) C,Cu 100.8(3,4.7) P,Cu 79.62(7,5.28) N,N 140.1(3) Pt,Pt 132.67(5)	[24]
[{$(Me)_2Pt(\mu$-η^3-$dppy)\}_2Cu$].BF_4.$0.5H_2O$ (red orange)	tr $P\bar{1}$ 2	11.3173(4) 13.7285(5) 22.1019(8)	96.287(1) 99.722(1) 111.279(1)	$Pt^{II}C_2P_2Cu$ $Cu^IN_2Pt_2$	MeC 2.10(1,3) $\mu\eta^3$P 2.308(2,2) 2.323(2,1) $\mu\eta^3$N 1.973(7,10)	Cu 2.595(1) 2.620(1)	C,C 81.9(4,2) P,P 99.18(8,1) C,Cu 100.7(3,4.2) P,Cu 83.24(6,0) N,N 138.8(3) Pt,Pt 134.27(5)	[24]
[{$(H_3N)_2Pt(\mu$-η^2-$NHCOMe)_2\}_2Ni$].$(ClO_4)_2$ (pale green)	m $P2/n$ 2	9.963(3) 7.356(2) 16.445(3)	90.91(2)	$Pt^{II}N_4Ni$ $Ni^{II}O_4Pt_2$	H_3N 2.08(2,1) $\mu\eta^2$N 2.00(2,1) η^2O 2.03(1,2)	Ni 2.611(1,0)	N,N 90.0(8,3.8) 176.5(2,2) O,O 89.8(6) Pt,Pt 180	[77]
[{$(H_3N)_2Pt(\mu$-η^2-$NHCOBu^t)_2\}_2Co$].$(ClO_4)_2$ (blue)	m $P2_1/n$ 2	13.451(2) 11.0189(19) 16.056(3)	97.477(3)	$Pt^{II}N_4Co$ $Co^{II}O_4Pt_2$	H_3N 2.050(6,5) $\mu\eta^2$N 1.991(6,0) $\mu\eta^2$O 2.038(4,15)	Co2.6197(4,0)	N,N 90.0(2,2.6) O,O 90.0(2,7) Pt,Pt 180.0	[76]
[{$(H_3N)_2Pt(\mu$-η^2-$pyo)_2\}_2Cu$].$(NO_3)_2$ (orange red)	or $Fdd2$ 8	23.281(4) 22.551(4) 10.852(2)		$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.03(1,1) $\mu\eta^2$N 2.024(9,9) $\mu\eta^2$O 1.960(9,9)	Cu 2.6312(4,0)	N,N 90.0(5,1.3) 174.6(4,3.9) N,Cu 87.4(3,3.1) O,O 162.1(3) O,Pt 86.0(2,10.0) Pt,Pt 175.3(1)	[78]
[{$(Me)NH_2)_2Pt(\mu$-η^2-$pyo)_2\}_2Cu$]$(NO_3)_2$ (orange-red)	m $P2_1/n$ 2	11.448(4) 18.771(2) 16.085(3)	105.18(2)	$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	N 2.058(5,4) $\mu\eta^2$N 2.028(5,5) $\mu\eta^2$O 1.973(4,10)	Cu 2.6320(8) 2.6450(8)	N,N 90.0(2,4.0) 176.9(2,2.7) N,Cu 88.8(1,6,8) O,O 90.0(2,3.3) 163.7(2,5) O,Pt 90.0(1,12.8) Pt,Pt 175.17(3)	[78]
[{$(H_3N)_2Pt(\mu$-η^2-$Meu)_2\}_2Pd$].$(NO_3)_3$.HNO_3.$5H_2O$ (blue-purple) (at 238 K)	tr $P\bar{1}$ 1	10.032(2) 10.160(2) 11.666(2)	103.33(1) 106.29(2) 96.03(1)	$Pt^{II}N_4Pd$ $Pd^{III}O_4Pt_2$	H_3N 2.046(7,3) $\mu\eta^2$N 2.029(7,5 $\mu\eta^2$O 1.980(7,18)	Pd 2.634(1,0)	N,N 90.0(3,5) 178.9(3,0) O,O 90.0(4,6) Pt,Pt 180	[79] [80]
[{$(H_3N)_2Pt(\mu$-η^2-$Meu)_2\}_2Pd$].$(NO_3)_3$.$11H_2O$ (blue-purple) (at 233 K)	tr $P\bar{1}$ 1	11.611(4) 10.083(2) 12.121(4)	109.19(2) 106.29(2) 99.73(2)	$Pt^{II}N_4Pd$ $Pd^{III}O_4Pt_2$	H_3N 2.051(8,1) $\mu\eta^2$N 2.032(8,6) $\mu\eta^2$O 1.992(7,6)	Pd 2.641(1,0)	N,N 90.0(3,2.0) 178.3(3,7) O,O 90.0(3,1.1) Pt,Pt 180	[79] [80]
[{$(\eta^2$-$en)Pt(\mu$-η^2-$Met)_2\}_2Pd$].$(NO_3)_3$.$12H_2O$ (blue-purple)	tr $P\bar{1}$ 1	10.270(1) 11.627(1) 12.274(1)	105.23(1) 102.87(1) 105.72(1)	$Pt^{II}N_4Pd$ $Pd^{III}O_4Pt_2$	η^2N 2.022(5,7) $\mu\eta^2$N 2.032(5,0) $\mu\eta^2$O 1.990(4,2)	Pd 2.645(1,0)	N,N 83.2(2)[c] 92.3(2,1.5) 176.0(2,6) O,O 90.0(2,9) Pt,Pt 180	[80]

Continued **Table 3.** Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[{$(H_3N)_2Pt(\mu$-η²-NHCOBu^t)$_2$}$_2$Mn].($ClO_4)_2.4H_2O$[d] (pale yellow)	m $P2_1/n$ 6	11.4228(17) 34.480(5) 16.128(3)	 91.481(3)	$Pt^{II}N_4Mn$ $Mn^{II}O_4Pt_2$ $Pt^{II}N_4Mn$ $Mn^{II}O_4Pt_2$	H_3N 2.048(13,23) $\mu\eta^2$N 2.013(11,6) $\mu\eta^2$O 2.092/(10,18) H_3N 2.031(16,25) $\mu\eta^2$N1.993(12,4) 2.031(12) $\mu\eta^2$O 2.044(8) 2.087(9,3)	Mn 2.6644(5,0) Mn 2.8807(18) 2.9995(18)	N,N 90.03(5,3.8) O,O 90.0(5,1.0) Pt,Pt 180.00 N,N 90.0(6,5.0) O,O 99.6(4,10.0) 145.4(4) Pt,Pt 114.12(6)	[76]
(NBu_4)[{$(C_6F_5)_2$.(η^2-acac)pt}$_2$Ag].CH_2Cl_2 (yellow)	m $P2_1/c$ 4	15.128(3) 19.414(4) 19.832(4)	 100.02(3)	$Pt^{II}O_2C_2Ag$ $Ag^{I}Pt_2$	η^2O 2.055(6,5) C 2.002(8,4)	Ag 2.668(1) 2.681(1)	O,O 91.5(2,5)[e] C,C 89.1(3,8) O,C 89.6(3,1.4) Pt,Pt 177.2(1)	[81]
[{$(H_3N)_2Pt(\mu$-η²-NHCOBu^t)$_2$}$_2$Cu].($ClO_4)_2$ (light green)	or Pbca 8	10.7665(17) 18.178(3) 19.570(3)		$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.055(5,3) $\mu\eta^2$N 1.990(5,5) $\mu\eta^2$O1.956(4,8)	Cu 2.6795(3,0)	N,N 90.0(2,2.8) O,O 90.0(1,8) Pt,Pt 180.0	[76]
[{$(H_3N)_2Pt(\mu$-η²-meu)(μ-η²-mec)}$_2$Cu].($NO_3)_4.6H_2O$ (blue)	tr $P\bar{1}$ 1	11.522(6) 10.924(4) 10.736(2)	91.51(3) 109.08(3) 114.43(3)	$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.074(14,7) $\mu\eta^2$uN 2.045(13) $\mu\eta^2$cN 2.036(11) $\mu\eta^2$uO 1.931(12) $\mu\eta^2$cO 1.988(9)	Cu 2.681(1,0)	N,N 90.0(5,1.6) 178.9(5,1) O,O 90.0(4,2.3) Pt,Pt 180	[82]
[{$(H_3N)_2Pt(\mu$-η²-meu)$_2$}$_2$Cu].$SO_4.8H_2O$	tg $I4_1/a$ 8	20.470(7) 23.509(8)		$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.046(12,1) $\mu\eta^2$N 2.015(14,4) $\mu\eta^2$O 1.936(12,7)	Cu 2.685(1,0)	N,N 90.0(6,1.2) 178.3(6,2) O,O 89.9(6) Pt,Pt 180	[83]
[{$(H_3N)_2Pt(\mu$-η²-NHCOBu)$_2$}$_2$Cu].($BF_4)_2$ (light breen)	m $P2_1/n$ 2	10.5401(7) 16.1012(11) 12.1744(8)	 110.352(1)	$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.053(6,6) $\mu\eta^2$N 2.014(5,3) $\mu\eta^2$O 1.959(4,1)	Cu 2.6957(3,0)	N,N 90.0(2,3.0) O,O 90.0(2,9) Pt,Pt 180.0	[76]
[{$(H_3N)_2Pt(\mu$-η²-met)$_2$}$_2$Mn].$Cl_2.10H_2O$ (colourless)	tr $P\bar{1}$ 1	11.788(6) 10.035(5) 10.983(6)	115.16(3) 103.22(4) 77.39(4)	$Pt^{II}N_4Mn$ $Mn^{II}O_4Pt_2$	H_3N2.038(20,17) $\mu\eta^2$,N2.019(20,3) $\mu\eta^2$,O2.130(17,28)	Mn 2.704(1,0)	N,N 90.0(8,1.2) 178.7(8,5) O,O 94.5(6) Pt,Pt 180	[84]
[{$(H_3N)_2Pt(\mu$-η²-NHCOMe)$_2$}$_2$Cu].($ClO_4)_2$ (green)	m $P2_1/n$ 2	9.924(1) 7.364(1) 16.589(2)	 91.08(1)	$Pt^{II}N_4Cu$ $Cu^{II}O_4Pt_2$	H_3N 2.050(5,1) $\mu\eta^2$N 2.003(5,8) $\mu\eta^2$O 1.949(3,0) 1.999(4,0)	Cu 2.765(2,0)	N,N 90.0(2,3.6) 177.3(2,1.4) O,O 90.1(2) Pt,Pt 180	[77]
(NBu_4)[{$(C_6F_5)_3$.Pt(μ-tht)}$_2$.Ag][d] (white) (at 233(1) K)	tr $P\bar{1}$ 2	13.486(3) 14.697(4) 17.333(4)	106.01(2) 90.50(2) 98.03(3)	$Pt^{II}C_3SAg$ $Ag^{I}S_2Pt_2$ $Pt^{II}C_3SAg$ $Ag^{I}S_2Pt_2$	C 2.022(6) 2.076(9,4) μS 2.326(2) μS 2.778(2,0) C 2.025(6) 2.075(8,4) μS 2.294(2) μS 2.547(2,0)	Ag 2.783(1,0) S 65.4(1) Ag 2.862(1,0) S 72.3(1)	C,C 88.7(3,2) 174.6(3) C,μS 91.4(2,3.7) 175.3(2) μS,Ag 65.8(1) μS,Pt 49.4(1) Pt,Pt 180 C,C 89.0(3,9) 174.9(3) C,μS 91.4(2,3) 170.3(2) μS,Ag 58.0(1) μS,Pt 49.8(1) Pt,Pt 180	[85]
[{$(Et_3P)(C_6Cl_5)$.Pt(μ-H)}$_2$Ag].CF_3SO_3 (colourless)	tr $P\bar{1}$ 2	13.853(3) 14.214(2) 15.611(3)	94.64(2) 90.48(2) 110.39(2)	$Pt^{II}P_2CHAg$ $Ag^{I}H_2Pt_2$	Et_3P2.320(5,14) C 2.06(1,1) μH 1.75(9) μH 1.70(-,12)	Ag 2.790(1,1) H 107(5,2)	PP 171.93(7,2) C,Ag 148.5(2,1.2) H,H 152(2) Pt,Pt 166.05(4)	[85]
[{$(H_3N)_2Pt(\mu$-η²-meu)$_2$}$_2$Pd].($ClO_4)_2.2.25H_2O$[d] (golden-tan)	tr $P\bar{1}$ 2	12.064(2) 12.524(1) 13.730(1)	80.05(1) 106.70(1) 108.62(1)	$Pt^{II}N_4Pd$ $Pd^{II}O_4Pt_2$ $Pt^{II}N_4Pd$ $Pd^{II}O_4Pt_2$	H_3N 2.059(10) $\mu\eta^2$N 2.033(8,1) $\mu\eta^2$O 2.015(8,2) H_3N 2.064(10,4) $\mu\eta^2$N 2.038(10,3) $\mu\eta^2$O 2.033(9,3)	Pd 2.837(1,0) Pd 2.839(1,0)	N,N 90.0(3,1.1) 178.9(3,3) O,O 90.0(3,1.0) Pt,Pt 180 N,N 90.0(4,3.0) 178.0(3,4) O,O 90.0(3,1.4) Pt,Pt 180	[80]

Continued **Table 3.** Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[{$(H_3N)_2Pt(\mu$-η^2-met)$_2$}$_2$Ag].(NO_3).5H_2O (colourless)	tr P$\bar{1}$ 2	14.122(11) 13.422(23) 11.747(12)	101.60(10) 100.01(8) 95.94(11)	$Pt^{II}N_4Ag$ $Ag^{I}O_4Pt_2$	H_3N 2.059(15,36) $\mu\eta^2$N 2.042(12,22) $\mu\eta^2$O 2.382(14,30) 2.522(12,41)	Ag 2.849(1) 2.884(1)	N,N 90.0(5,2.1) 178.0(5,0) O,O 82.7(4,3.6) 155.8(4,3.8) Pt,Pt 145.11(5)	[87]
[{(η^2-dpae)(Me)Pt.(μ-Cl)}$_2$Ag].BF_4.0.5thf (red)	tr P$\bar{1}$ 2	10.5016(3) 17.9476(5) 18.7605(5)	109.92(1) 90.684(1) 91.212(1)	$Pt^{II}N_2CClAg$ $Ag^{I}Cl_2Pt_2$.	η^2N 2.011(2,5) 2.092(2,2) MeC 2.082(3,18) μCl 2.294(1,4) μCl 2.434(1,37)	Ag 2.895(1,0) Cl 74.64(3) 113.34(5)	N,N 77.3(1,1)[c] C,μCl 88.1(1) N,C 97.7(1,5) Cl,Cl 164.87(5)	[88]
[{(η^2-Me_4en)Pt.(μ-η^2-meu)$_2$}$_2$ Cu](ClO$_4$)$_2$ (bright green)	tr P$\bar{1}$ 1	10.127(1) 10.816(2) 12.317(2)	68.54(1) 65.75(1) 89.52(2)	$Pt^{II}N_4Cu$ $Cu_{II}O_4Pt_2$	η^2N2.087(3,15) $\mu\eta^2$N2.048(3,15) $\mu\eta^2$O 1.931(3,5)	Cu 2.9843(1,0)	N,N 84.2(1)[c] 91.9(1,5.2) 176.4(1,6) O,O 90.0(1,1.1)	[89]
B: Pt-Pt-M								
[(xylNC)(μ-H)Pt_2.(μ-η^3-dpmp)$_2$Pd..(xylNC)](BF$_4$)$_3$.3.5CH_2Cl_2.4H_2O (red) (at 135 K)	tr P$\bar{1}$ 2	18.147(7) 19.881(7) 14.850(5)	99.82(4) 101.03(4) 93.17(5)	$Pt^{II}P_2H$ PdPt $Pt^{II}P_2HCPt$ $Pd^{II}P_2CPt$	$\mu\eta^3$P 2.290(7,10) μH not given $\mu\eta^3$P 2.336(7,14) μH not given C 2.03(3) $\mu\eta^3$P 2.318(7,24) C 2.13(4)	Pd 2.634(3) Pt 2.867(2)	P,P 174.2(3) P,Pd 87.4(2,1.2) P,Pt 92.5(2,1.3) Pd,Pt 174.41(7) P,P 175.9(3) P,Pt 88.6(2,1.2) C,Pt 148.8(9) P,P 179.1(3) P,Pt 90.4(2,2.2) C,Pt 174.0(9)	[90]
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.Pd(xylNC)].(PF_6)$_2$.4Me_2CO (red)	tr P$\bar{1}$ 1	13.906(7) 16.084(7) 11.858(7)	95.68(4) 110.09(4) 76.68(4)	PtP_2M_2 MP_2CPt (x2)	$\mu\eta^3$P 2.262(2,0) $\mu\eta^3$P 2.293(3.1) C 1.992(9)	M 2.690(2,0)	P,P180.00 P,M 90.0(-,4.7) M,M 180.00 P,P 160.55(8) P,Pt 85.9(-,1.1) C,Pt 166.9(3)	[58] [91]
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.Rh(Cl)(xylNC)].(PF_6)$_2$.2CH_2Cl_2 (orange) (at 193 K)	m P2$_1$/c 4	24.95(2) 15.772(1) 25.526(4)	 119.20(1)	$Pt^{II}P_2RhPt$ $Pt^{II}P_2CPt$ $Rh^{I}P_2CClPt$	$\mu\eta^3$P 2.265(1,4) $\mu\eta^3$P 2.315(1,8) C 1.947(6) $\mu\eta^3$P 2.313(1,21) C 1.884(6) Cl 2.358(1)	Rh 2.7537(5) Pt 2.6588(3)	P,P 176.74(5) P,Rh 91.62(4,3.0 P,Pt 88.37(4,23) Pt,Rh 177.13(1) P,P 178.43(5) P,C 89.3(2,3) P,Pt 90.68(3,36) P,Pt 89.20(4,5.4) C,Pt 77.8(2) Cl,Pt 105.72(4)	[92] [93]
[(xylNC)Pt_2(μ-CO).(μ-η^3-dpmp)$_2$.Rh(Cl)(xylNC)].(PF_6)$_2$.2.5CH_2Cl_2 (orange) (at 155 K)	or Pbca 8	39.94(1) 23.964(7) 19.534(4)		$Pt^{II}P_2CRhPt$ $Pt^{II}P_2CPt$ $Rh^{I}P_2C_2ClPt$	μP 2.276(6,21) μOC 2.16(2) $\mu\eta^3$P 2.316(6,10) C 1.94(2) $\mu\eta^3$P 2.335(7,20) C 1.84(2) μOC 1.90(2) Cl 2.468(7)	Rh 2.762(2) C 85.4(8) Pt 2.667(1)	P,P 169.1(2) P,Rh 93.0(2,1.6) P,Pt 85.8(2,2.3) Rh,Pt 163.85(5) P,P 174.3(2) P,C 91.6(6,5) P,Pt 88.5(2,2.1) C,Pt 176.3(6) P,Pt 92.7(2,7) C,Pt 168.7(7) μC,Pt 51.2(6) Cl,Pt 79.6(2)	[93]
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.Ir(Cl)(xylNC)].(PF_6)$_2$ (orange)	tr P$\bar{1}$ 2	15.987(6) 22.041(6) 15.145(7)	103.31(3) 95.86(4) 74.68(2)	$Pt^{II}P_2IrPt$ $Pt^{II}P_2CPt$ $Ir^{I}P_2CClPt$	$\mu\eta^3$P 2.263(7,5) $\mu\eta^3$P 2.316(7,2) C 2.01(2) $\mu\eta^3$P 2.318(7,5) C 1.90(2) Cl 2.356(6)	Ir 2.765(2) Pt 2.652(2)	P,P 175.6(2) P,Ir 91.8(2,2.9) P,Pt 88.2(2,5) Ir,Pt 177.58(7) P,P 179.3(2) P,C 89.8(7,1.0) P,Pt 90.2(2,7) C,Pt 179.4(6) P,Pt 88.5(2,5.9) C,Pt 81.1(7) Cl,Pt 106.1(2)	[93]

Continued **Table 3.** Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.Rh(Cl)(xylNC)$_2$].(PF_6)$_2$.4CH_2Cl_2 (orange) (at 136 K)	tr P$\bar{1}$ 2	15.633(4) 24.722(8) 14.569(7)	101.46(4) 109.77(3) 89.15(3)	$Pt^{II}P_2RhPt$	$\mu\eta^3$P 2.279(5,3)	Rh 2.797(2) Pt 2.694(1)	P,P 173.7(2) P,Rh 92.7(1,2.2) P,Pt 87.3(1,6) Rh,Pt 178.02(5)	[93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.328(5,2) C 1.90(1)		P,P 177.3(2) P,C 90.0(4,3.2) P,Pt 90.0(1,5) C,Pt 176.8(4)	
				$Rh^{II}P_2C_2$.ClPt	$\mu\eta^3$P 2.348(5,21) C 1.96(2,4) Cl 2.502(6)		P,Pt 87.8(1,5.3) C,Pt 71.2(5) 102.0(6) Cl,Pt 161.1(1)	
[(mesNC)Pt_2.(μ-η^3-dpmp)$_2$.Ir(mesNC)$_3$].(PF_6)$_3$.2CH_2Cl_2 (at 156 K)	m $P2_1/n$ 4	20.111(5) 22.153(4) 25.835(5)	99.27(2)	$Pt^{II}P_2IrPt$	$\mu\eta^3$P 2.253(3,7)	Ir 2.8195(8) Pt 2.6908(8)	P,P 173.7(1) P,Ir 93.11(9,1.4) P,Pt 86.86(9,68) Ir,Pt 176.48(3)	[93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.305(4,0) C 1.99(1)		P,P 179.0(1) P,C 90.4(3,3) P,Pt 89.60(8,6.7) C,Pt 178.7(3)	
				$Ir^{II}C_3P_2Pt$	C 1.97(2,1) 2.06(1) $\mu\eta^3$P 2.341(4,17)		C,Pt 71.9(4) 100.6,163.0(3) P,Pt 86.13(9,4.4)	
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.CuBr]((PF_6)$_2$.Et_2O (yellow) (at 178 K)	m $P2_1/c$ 4	14.910(4) 21.891(7) 27.226(8)	101.66(6)	$Pt^{II}P_2CCuPt$	$\mu\eta^3$P 2.283(3,2) C 2.01(1)	Cu 2.857(1) Pt 2.7180(5)	P,P 173.96(9) P,C 88.5(3,3) P,Pt 91.76(6,8) C,Pt 173.1(3) Cu,Pt 98.09(3)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.296(3,2) C 1.94(1)		P,P 172.74(9) P,C 87.3(3,3) P,Pt 92.64(6,17) C,Pt 179.1(3)	
				$Cu^{I}P_2BrPt$	$\mu\eta^3$P 2.265(3,11) Br 2.412(2)		P,P 137.0(1) P,Br 110.94(8,4.0) Br,Pt 85.94(4)	
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.CuI]((PF_6)$_2$.Et_2O (yellow)	m $P2_1/c$ 4	15.048(4) 21.922(3) 27.840(3)	101.89(1)	$Pt^{II}P_2CCuPt$	$\mu\eta^3$P 2.290(5,3) C 2.06(1)	Cu 2.863(2) Pt 2.715(1)	P,P 174.1(2) P,C 88.3(5,7) P,Pt 91.9(1,3) C,Pt 173.1(4) Cu,Pt 97.96(5)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.309(5,6) C 1.90(2)		P,P 169.7(2) P,C 87.2(5,1.7) P,Pt 92.8(1,3) C,Pt 178.1(5)	
				$Cu^{I}P_2IPt$	$\mu\eta^3$P 2.281(5,15) I 2.597(2)		P,P 136.5(2) P,I 111.1(1,3.1) I,Pt 87.75(7)	
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.CuCl]((PF_6)$_2$.Et_2O (yellow)	m $P2_1/c$ 4	15.037(4) 22.081(6) 27.449(4)	101.92(2)	$Pt^{II}PCCuPt$	$\mu\eta^3$P 2.290(3,2) C 2.01(1)	Cu 2.872(1) Pt 2.7273(8)	P,P 173.45(9) P,C 93.2(3,5.0) P,Pt 91.66(7,2) C,Pt 172.7(3)	[94]
				$Cu^{I}P_2CPt$	$\mu\eta^3$P 2.302(3,1) C 1.95(1)		P,P 173.4(1) P,C 87.1(3,1) P,Pt 92.78(7,3) C,Pt 178.6(3)	
				$Cu^{I}P_2ClPt$	$\mu\eta^3$P 2.271(3,11) Cl 2.276(3)		P,P 136.5(1) P,Cl 110.2(1,1.9) Cl,Pt 85.92(8)	

Continued Table 3. Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[(xylNňC)Pt_2.(μ-η^3-dpmp)$_2$.Ir(Cl)(xylNC)].(PF_6)$_2$ (orange)	tr P$\bar{1}$ 2	15.987(6) 22.041(6) 15.145(7)	103.31(3) 95.86(4) 74.68(2)	$Pt^{II}P_2IrPt$	$\mu\eta^3$P 2.263(7,5)	Ir 2.765(2) Pt 2.652(2)	P,P 175.6(2) P,Ir 91.8(2,2.9) P,Pt 88.2(2,5) Ir,Pt 177.58(7)	[93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.316(7,2) C 2.01(2)		P,P 179.3(2) P,C 89.8(7,1.0) P,Pt 90.2(2,7) C,Pt 179.4(6)	
				$Ir^{I}P_2CClPt$	$\mu\eta^3$P 2.318(7,5) C 1.90(2) Cl 2.356 (6)		P,Pt 88.5(2,5.9) C,Pt 81.1(7) Cl,Pt 106.1(2)	
[(xylNC)Pt_2.(μ-η^3-dpmp)$_2$.Rh(Cl) (xylNC)$_2$].(PF_6)$_2$.4C H_2Cl_2 (orange) (at 136 K)	tr P$\bar{1}$ 2	15.633(4) 24.722(8) 14.569(7)	101.46(4) 109.77(3) 89.15(3)	$Pt^{II}P_2RhPt$	$\mu\eta^3$P 2.279(5,3)	Rh 2.797(2) Pt 2.694(1)	P,P 173.7(2) P,Rh 92.7(1,2.2) P,Pt 87.3(1,6) Rh,Pt 178.02(5)	[93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.328(5,2) C 1.90(1)		P,P 177.3(2) P,C 90.0(4,3.2) P,Pt 90.0(1,5) C,Pt 176.8(4)	
				$Rh^{II}P_2C_2$.ClPt	$\mu\eta^3$P 2.348(5,21) C 1.96(2,4) Cl 2.502(6)		P,Pt 87.8(1,5.3) C,Pt 71.2(5) 102.0(6) Cl,Pt 161.1(1)	
[(mesNC)Pt_2.(μ-η^3-dpmp)$_2$.Ir(mesNC)$_3$].(PF_6)$_3$.2CH_2Cl_2 (at 156 K)	m P2$_1$/n 4	20.111(5) 22.153(4) 25.835(5)	99.27(2)	$Pt^{II}P_2IrPt$	$\mu\eta^3$P 2.253(3,7)	Ir 2.8195(8) Pt 2.6908(8)	P,P 173.7(1) P,Ir 93.11(9,1.4) P,Pt 86.86(9,68) Ir,Pt 176.48(3)	[93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.305(4,0) C 1.99(1)		P,P 179.0(1) P,C 90.4(3,3) P,Pt 89.60(8,67) C,Pt 178.7(3)	
				$Ir^{II}C_3P_2Pt$	C 1.97(2,1) 2.06(1) $\mu\eta^3$P 2.341(4,17)		C,Pt 71.9(4) 100.6,163.0(3) P,Pt 86.13(9,4.4)	
[(xylNC)$_2$$Pt_2$.($\mu$-$\eta^3$-dpmp)$_2$.CuBr](($PF_6$)$_2$.$Et_2O$ (yellow) (at 178 K)	m P2$_1$/c 4	14.910(4) 21.891(7) 27.226(8)	101.66(6)	$Pt^{II}P_2CCuPt$	$\mu\eta^3$P 2.283(3,2) C 2.0(1)	Cu 2.857(1) Pt 2.7180(5)	P,P 173.96(9) P,C 88.5(3,3) P,Pt 91.76(6,8) C,Pt 173.1(3) Cu,Pt 98.09(3)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.296(3,2) C 1.94(1)		P,P 172.74(9) P,C 87.3(3,3) P,Pt 92.64(6,17) C,Pt 179.1(3)	
				$Cu^{I}P_2BrPt$	$\mu\eta^3$P 2.265(3,11 Br 2.412(2)		P,P 137.0(1) P,Br 110.94(8,4.0) Br,Pt 85.94(4)	
[(xylNC)$_2$$Pt_2$.($\mu$-$\eta^3$-dpmp)$_2$.CuI](($PF_6$)$_2$.$Et_2O$ (yellow)	m P2$_1$/c 4	15.048(4) 21.922(3) 27.840(3)	101.89(1)	$Pt^{II}P_2CCuPt$	$\mu\eta^3$P 2.290(5,3) C 2.06(1)	Cu 2.863(2) Pt 2.715(1)	P,P 174.1(2) P,C 88.3(5,7) P,Pt 91.9(1,3) C,Pt 173.1(4) Cu,Pt 97.96(5)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.309(5,6) C 1.90(2)		P,P 169.7(2) P,C 87.2(5,1.7) P,Pt 92.8(1,3) C,Pt 178.1(5)	
				$Cu^{I}P_2IPt$	$\mu\eta^3$P 2.281(5,15) I 2.597(2)		P,P 136.5(2) P,I 111.1(1,3.1) I,Pt 87.75(7)	

Continued Table 3. Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$[(xylNC)_2Pt_2(\mu\text{-}\eta^3\text{-}dpmp)_2CuCl](PF_6)_2\cdot Et_2O$ (yellow)	m $P2_1/c$ 4	15.037(4) 22.081(6) 27.449(4)	101.92(2)	$Pt^{II}P_2CCuPt$	$\mu\eta^3$P 2.290(3,2) C 2.01(1)	Cu 2.872(1) Pt 2.727(8)	P,P 173.45(9) P,C 93.2(3,5.0) P,Pt 91.66(7,2) C,Pt 172.7(3) Cu,Pt 97.74(3)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.302(3,1) C 1.95(1)		P,P 173.4(1) P,C 87.1(3,1) P,Pt 92.78(7,3) C,Pt 178.6(3)	
				$Cu^{I}P_2ClPt$	$\mu\eta^3$P 2.271(3,11) Cl 2.276(3)		P,P 136.5(1) P,l 110.2(1,1.9) Cl,Pt 85.92(8)	
$[(xylNC)Pt_2(\mu\text{-}\eta^3\text{-}dpmp)_2(\mu\text{-}Cl)Rh(xylNC)](PF_6)_2\cdot 4CH_2Cl_2$ (orange) (at 178 K)	m Pn 2	14.892(7) 20.813(6) 16.742(3)	113.50(2)	$Pt^{II}P_2Cl.$ RhPt	$\mu\eta^3$P 2.265(5,18) μCl 2.563(5)	Rh 2.967(2) Cl 73.3(1) Pt 2.644(1)	P,P 172.0&(2) P,μCl 86.6(2,6.1) P,Rh 89.5(1,4.6) μCl,Rh 50.9(4) Rh,Pt 125.21(4)	[92] [93]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.289(5) 2.330(5) C 1.85(1)		P,P 177.8(2) P,C 89.6(6,3) P,Pt 90.4(1,2.5) C,Pt 177.8(6)	
				$Rh^{II}P_2CClPt$	$\mu\eta^3$P 2.306(5,17) C 1.86(2) μCl 2.406(4)		P,Pt 91.3(1,4.5) C,Pt 118.5(6) μCl,Pt 55.8(1)	
$[(xylNC)Pt_2(\mu\text{-}\eta^3\text{-}dpmp)_2Au](PF_6)_3\cdot Me_2CO$	m $P2_1/n$ 4	15.147(3) 25.947(8) 25.759(6)	104.10(2)	$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.312(7,14) C 2.08(8)	Au 3.045(2) Pt 2.708(2)	P,P 175.6(3) P,C 90.0(6,1.9) P,Au 87.9(2,4.6) C,Au 73.0(6) Au,Pt 110.68(5)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.300(8,23) C 1.90(3)		P,P 177.8(3) P,C 88.9(8,4.7) P,Pt 91.1(2,3.7) C,Pt 178.5(8)	
				$Au^{I}P_2Pt$	$\mu\eta^3$P 2.338(7,11)		P,P 172.9(3) P,Pt 90.1(2,3.3)	
$[(xylNC)Pt_2(\mu\text{-}\eta^3\text{-}dpmp)_2Ag](PF_6)_3$	m C2/c 8	18.302(6) 25.056(6) 47.172(9)	99.11(3)	$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.285(9,4) C 1.98(3)	Ag 3.118(3) Pt 2.657(2)	P,P 160.9(3) P,C 96.9(9,1.9) P,Ag 87.1(2,3.8) C,Ag 64.1(9) Ag,Pt 136.36(8)	[94]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.31(1,1) C 1.93(3)		P,P 176.0(3) P,C 90.4&(9,2.3) P,Pt 89.4(2,3.9) C,Pt 173.3(9)	
				$Ag^{I}P_2Pt$	$\mu\eta^3$,P 2.40(1,0)		P,P 176.9(3) P,Pt 89.9(2,2.0)	
$[(xylNC)Pt_2(\mu\text{-}\eta^3\text{-}dpmp)(\mu\text{-}\eta^3\text{-}dpmpd)Pd(xylNC)](PF_6)_2\cdot 2CH_2Cl_2$ (yellow) (at 155 K)	tr $P\bar{1}$ 2	18.949(4) 19.555(4) 14.328(3)	96.81(2) 110.01(1) 106.52(2)	$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.292(2) $\mu\eta^3$P 2.226(2) μC 2.138(7)	Pd 3.3453(7) C 105.4(3) Pt 2.6792(4)	P,P165.78(7) P,μC 95.5(2,20) P,Pt 86.81(5,1.9) μC,Pt 155.3(2)	[90]
				$Pt^{II}P_2CPt$	$\mu\eta^3$P 2.287(2,13) C 1.983(8)		P,P 168.85(7) P,Pt 90.29(5,2.3) C,Pt 160.3(2)	
				PdC_3P	NC 1.999(8) $\mu\eta^3$C 2.144(7) $\mu\eta^3,\mu$C 2.067(7) $\mu\eta^3$P 2.295(2)		C,C 113.6(3) C,μC 40.8(3)^{i} 154.2(3) μC,P 105.0(2)	

Continued **Table 3.** Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[(xylNC)Pt_2.(μ-η^3-dpmp).(μ-η^3-dpmpe).Pd(xylNC)].(PF_6)$_2$.4CH_2Cl_2 (yellow) (at 155 K)	m $P2_1/a$ 4	27.465(9) 12.246(3) 31.06(1)	 103.50(4) 	$Pt^{II}P_2CPt$ $Pt^{II}P_2CPt$ PdC_3P	$\mu\eta^3$P 2.274(2) $\mu\eta^3$P 2.239(5) μC 2.04(2) $\mu\eta^3$P 2.283(5,1) C 1.93(2) C 1.98(2) $\mu\eta^3$C 2.06(2) μC 2.16(2) $\mu\eta^3$P 2.279(6)	Pd 3.590(2) C 117.4(8) Pt 2.696(1)	P,P 171.7(2) P,μC 94.1(5,9) P,Pt 86.0(1,1.7) μC,Pt 168.9(5) P,P 174.0(2) P,Pt 88.1(1,6) C,Pt 171.7(4) C,C 114.7(8) C,μC 38.8(7)[f] 153.1(7) μC,P 101.1(5)	[90]
[(xylNC)Pt_2.(μ-η^3-dpmp).(μ-η^3-dpmpm).Pd(xylNC)].(PF_6)$_2$.4.5CH_2Cl_2 (yellow) (at 155 K)	tr $P\bar{1}$ 2	14.518(3) 30.086(3) 11.631(3)	92.55(2) 96.55(4) 90.44(4)	$Pt^{II}P_2CPt$ $Pt^{II}P_2CPt$ PdC_3P	$\mu\eta^3$P 2.298(3) $\mu\eta^3$P 2.246(3) μC 2.119(9) $\mu\eta^3$P 2.283(3,1) C 1.98(1) C 2.02(1) $\mu\eta^3$C 2.11(1) μC 2.11(1) $\mu\eta^3$P 2.295(3)	Pd 3.6377(9) C 118.7(5) Pt 2.6993(7)	P,P 170.2(1) P,μC 94.4(3,9) P,Pt 85.81(7,1.36) μC,Pt 95.3(3) P,P 168.2(1) P,Pt 88.81(7,3.43) C,Pt 167.3(3) C,C 112.1(4) C,μC 39.3(4)[f] 151.1(4) μC,P 105.9(3)	[90]
C: UNIQE STRUCTURES								
(Et_3P)$_4$(Cl)Pt_2.μ-η^1: η^2-C≡P).W(CO)$_5$ (orange) (at 173(2) K)	m $P2_1/n$ 4	11.0994(2) 33.5717(2) 12.4301(1)	 111.659(1) 	PtP_3C PtP_2CCl WC_5P	Et_3P not given μC 2.104(9) μP 2.292(3) Et_3P not given μC 1.952(9) Cl not given OC not given μP 2.531(3)	 	not given not given not given	[95]
[(Me_3Pt)$_2${μ-η^2-O_2.S(O)CF_3}$_3$Ag.(η^2-tol)$_2$] (white)	m $P2_1/n$ 4	11.476(4) 19.761(5) 15.831(4)	 93.84(4) 	$Pt^{IV}O_3C_3$ $Ag^{I}C_4O_2$	O 2.269(7) MeC 2.003(12) η^2C 2.389(12,4) 2.63(2,6) $\mu\eta^2$O 2.481(8,26)	 	C,C 89.1(6) O,O 84.4(3)	[96]
[(η^2-dppe)$_2Pt_2$.(μ-C≡CPh)$_4$Cu].BF_4 (colourless)	m $P2_1/c$ 4	16.259(7) 19.312(9) 27.241(8)	 105.98(3) 	$Pt^{II}C_2P_2$ $Cu^{I}C_8$	μC 2.02(3,3) η^2P 2.278(10,5) C 2.43(3,6) μC 2.24(3,5)	Cu 3.088(5) 3.133(5)	μC,μC 92(1,2) P,P 86.8(3,4)[c] μC,P 91(1,3) not given	[97]
[(Ph_3P)$_4Pt_2$.(μ-C≡CPh)$_4$.Ag]ClO_4.2$CHCl_3$ (white) (at 200(1) K)	tr $P\bar{1}$ 2	14.933(2) 17.783(3) 19.058(2)	80.60(1) 84.09(1) 74.98(1)	$Pt^{II}C_2P_2$ $Ag^{I}C_8$	μC 2.006(7,2) 2.033(8) Ph_3P 2.316(2,12) C 2.537(8,40) 2.648(8,55) μC 2.436(8,70) 2.609(7,26)	Ag 3.384(1) 3.513(1)	μC,μC 88.8(3,3) P,P 97.35(7,42) μC,P 86.9(2,3.6) C,C not given	[98]
(Ph_3P)$_2$Pt(μ-OH)$_2$.Pd(μ-PPh_2)$_2$Pt.(C_6F_5)$_2$ (yellow)	m C2/c 8	19.092(2) 22.742(2) 31.810(2)	 93.48(1) 	$Pt^{II}O_2P_2$ $Pt^{II}C_2P_2$ $Pd^{II}O_2P_2$	μO 2.067(6,22) Ph_3P 2.232(3,6) C 2.072(11,8) μC 2.298(3,18) μO 2.161(6,33) μP 2.242(3,17)	Pd 3.273(1,2) O 101.4(3,2.9) Pd 3.562(1) P 103.3(1,1.1)	μO,μO 79.3(3) P,P 97.9(1) μO,P 91.4(2,1.1) 170.5(2,1.3) C,C 90.3(4) μP,μP 74.1(1) C,μP 97.8(3,3.4) 170.8(2,4.3) μO,μO 75.2(2) μP,μP 76.3(1) μO,μP 104.1(2,5.1) 173.6(2,4)	[99]
[(η^2-Et_2NCS_2)Pt.(μ-η^2-$POPh_2$)$_2$Co.(μ-η^2-$POPh_2$)$_2$Pt.(η^2-Et_2NCS_2)].2$CHCl_3$ (dark blue)	m C2/c 4	25.798 11.31 26.270	 114.26 	$Pt^{II}S_2P_2$ $Co^{II}O_4$	η^2S 2.375(9,14) $\mu\eta^2$P 2.247(8,18) $\mu\eta^2$O 1.959(18,11)	 	S,S 74.0(3,1)[g] P,P 91.0(3,1) S,P 97.5(3,8) O,O 101.0(8,1.0) 114.0(9,3,1)	[100]

Continued **Table 3.** Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[(η²-Prⁱ₂NCS₂)Pt.(μ-η²-POPh₂)₂Co.(μ-η²-PSPh₂)₂Pt.(η²-Prⁱ₂NCS₂)] (blue)	m C2/c 4	29.168(23) 9.693(15) 24.467(15)	 101.13(4) 	$Pt^{II}S_2P_2$ $Co^{II}O_2S_2$	η²S 2.360(5,18) μη²P 2.253(4,11) μη²O 1.884(11) μη²S 2.319(4)	 	S,S 73.8(16)[g] P,P 93.30(13) S,P 96.5(1,2.3) 170.1(1,2.4) O,O 99.7(5) S,S 106.06(14) O,S 112.9(3,6.3)	[101]
$(C_6F_5)_2Pt(\mu$-C≡CSiMe$_3)_2$Pt.(μ-C≡CSiMe$_3)_2$.Rh(PEt$_3$)(η⁵-cp*) (yellow)	or Pca2$_1$ 4	27.588(2) 10.4447(9) 20.230(2)	 	$Pt^{II}C_6$ PtC_6 RhC_7P	C 2.311(14,30) μC 1.93(2,1) 2.35(2,4) C 2.03(2,0) C 2.317(15,14) μC 2.35(2,1) η⁵cp*C 2.24(2,5) μC 1.99(2,3) Et$_3$P 2.287(3)	Rh 3.297(1) C not given Pt 3.366(1) C not given	μC,μC 78.2(5) 106.4(6,2.1) 160.6(6,1.9) μC,C 89.1(6,7) 165.9(6,1.5) μC,C 104.6(5,2.3) 160.7(6,4.1) μC,μC 76.9(5) μC,P 88.4(4,3)	[102]
[{(η²-dach)Pt.(μ-η²:η² -betmp)}$_2$Cu](BF$_4)_2$ (blue)	tr P$\bar{1}$ 2	10.289(3) 11.209(2) 11.752(3)	96.8(2) 112.58(2) 111.33(2)	$Pt^{II}N_2S_2$ $Cu^{II}O_4$				[103]
[{(Ph$_3$P)$_2$Pt.(μ-η²:η²-deadt)}$_2$.Cu(OClO$_3)_2$] (green) (at 173 K))CuCl	tr P$\bar{1}$ 1	12.2246(10) 13.1026(10) 13.6811(10)	71.672(10) 80.366(10) 77.556(10)	$Pt^{II}S_2P_2$ $Cu^{II}O_6$	μη²S 2.344(2,16) Ph$_3$P 2.289(2,10) μη²O 1.904(6,13) O_3ClO 2.715(9)	 	S,S 73.14(8)[g] P,P 98.41(8) S,P 94.16(8,7) O,O 90.0(3)[e] 95.9(3,3.5)	[104]
[{(Et$_3$P)$_2$Pt}$_2$.{μ-η²:η²:η⁴-pz(b$_2$:d$_2$)}Ni] C$_6$H$_4$Cl$_2$ (blue)	m P2$_1$/c 2	13.006(4) 18.645(8) 14.469(6)	 105.86(3) 	$Pt^{II}S_2P_2$ $Ni^{II}N_4$	μη²S 2.333(3,3) Ph$_3$P 2.289(2,4) μη⁴N 1.886(5,8)	Ni 7.18 Pt 14.36 	S,S 89.86(6)[c] P,P 97.47(6) N,N 90.0(2,4)[e]	[105]
[{(η⁴-cod)ClPt}$_2$(μ-η¹:η⁵-C$_5$H$_4)_2$Ru] (colourless)	m P2$_1$/c 4	12.515(2) 10.170(2) 18.961(2)	 93.70(1) 	PtC_5Cl RuC_{10}	η⁴C 2.14(1,2) 2.27(1,1) μC 2.030(9,1) Cl 2.329(3,13) not given	 	C, C 36.4(5,1.6)[f] 81.3(5,6) C,μC 92.6(4,2.1) μC,Cl 91.5(3,4 not given	[106]
[{(Ph$_3$P)$_2$ClPt}$_2$.(μ-OH)(μ-η¹:η⁵-C$_5$H$_4)_2$Fe][d] (green)	m P2$_1$/a 4	18.36(1) 17.64(2) 38.313(8)	 97.04(3) 	PtIIOCClP FeC_{10}	μO 2.13(1) μC 2.00(1,1) Cl 2.386(5,0) Ph$_3$P 2.232(5,9) not given	Fe 3.727(3,2) Pt 3.990(2) O 138.9(2)	μO,C 92.1(5,9) μO,Cl 83.1(3,4) μO,P 174,9(3,2.4) not given	[107]
[{(Ph$_3$P)(py)ClPt}$_2$.(μ-η¹:η⁵-C$_5$H$_4)_2$Fe] (red orange)	m P2$_1$/c 4	10.22(2) 24.907(7) 22.175(9)	 96.00(7) 	$Pt^{II}CNClP$ FeC_{10}	μC 2.026(1,1) pyN 2.15(1,0) Cl 2.361(4,1) Ph$_3$P 2.212(4,4) not given	 	not given not given	[107]
[{(Ph$_3$P)$_2$ClPt}$_2$.(μ-SC$_6$H$_5$).(μ-η¹:η⁵-C$_5$H$_4)_2$.Fe].2Cl(CH$_2)_2$Cl (green)	or Pna2$_1$ 4	17.719(1) 15.888(2) 18.880(3)	 	$Pt^{II}CClSP$ FeC_{10}	μC 2.02(3,9) Cl 2.39(1,1) μS 2.38(2,5) Ph$_3$P 2.25(1,4) not given	Fe 3.767(7) Pt 4.057(1) S 116.8(2)	μC,μS 86(1,2) μC,P 90(1,1) μS,Cl 95.8(4,2) Cl,P 89.0(4,8) not given	[108]
[{(η²-CH$_2$=CH$_2$)Cl$_2$.Pt}$_2$(μ-η¹:η⁵-py cp*)$_2$Fe]CH$_2$Cl$_2$ (red)	m P2$_1$/c 2	9.436(2) 11.208(2) 17.980(4)	 97.44(2) 	$Pt^{II}C_2Cl_2N$ FeC_{10}	η²C 2.18(2.1) Cl 2.283(6,13) μη¹N 2.08(1) not given	 	C,C 38(1)[f] Cl,Cl 87.4 (7) C,Cl 91.0(7,5) C,N 160.9(9,3.9) Cl,N 90.0(4,1) not given	[109]
[{(η²-CH$_2$=CH$_2$)Cl$_2$.P t}$_2$(μ-η¹:η⁵-pycp)$_2$Fe]$_2$ (red)	m P2$_1$/n 4	13.858(9) 13.128(3) 14.807(1)	 90.13(1) 	$Pt^{II}C_2Cl_2N$ FeC_{10}	η²C 2.15(2,2) Cl 2.285(4,3) μη¹N 2.079(8) not given	 	C,C 37.0(7)[f] Cl,Cl 176.9(1) C,Cl 90.8(6,1.8) C,N 161.5(5,7) Cl,N 89.0(3,1.3) not given	[110]

Continued Table 3. Crystallographic and structural data for heterotrinuclear Pt_2M (M = transition metal) with linear metal array and an unique structures[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[{Cl_2(dmso)Pt}$_2$-(μ-η^1:η^5-dmat)$_2$Fe] (yellow)	m $P2_1/n$ 2	7.623(2) 13.993(4) 13.271(3)	 95.66(2) 	$Pt^{II}C_2NS$ FeC_{10}	Cl 2.303(2,1) $\mu\eta^1$N 2.143(7) dmsoS 2.229(3) not given		Cl,Cl 178.1(1) N,S 176.2(2) Cl,N 90.9(2,1.8) Cl,S 89.1(1,1.0) not given	[111]
[{Br(dmso)Pt}$_2$-(μ-η^2:η^5-dmat)$_2$Fe] (yellow)	m $P2_1/c$ 2	14.277(56) 8.974(3) 10.951(2)	 105.77(2) 	$Pt^{II}CNSBr$ FeC_{10}	$\mu\eta^2\mu$C 1.998(9) N 2.145(8) dmsoS 2.194(3) Br 2.537(1) not given		μC,N 81.5(4)[c] S,Br 91.2(1) μC,S 94.9(3) N,S 175.9(2) μC,Br 172.4(3) not given	[111]
[{Br(dmso)Pt}$_2$-(μ-η^2:η^5-dmat)$_2$Fe] (orange)	m $P2_1/c$ 4	9.984(3) 10.335(3) 25.929(7)	 92.28(2) 	$Pt^{II}CNSBr$ FeC_{10}	$\mu\eta^2\mu$C 1.97(2) N 2.14(1) dmsoS 2.202(5) Br 2.523(2) not given		μC,N 80.8(6)[c] S,Br 90.6(1) μC,S 95.5(5) N,S 175.2(4) V 173.8(4) not given	[111]
[{Cl(dmso)Pt}$_2$-(μ-η^2:η^5-dmat)$_2$Fe] (orange)	m $P2_1/c$ 4	9.910(4) 10.331(4) 25.532(11)	 91.99(3) 	$Pt^{II}CNSCl$ FeC_{10} not given	$\mu\eta^2\mu$C 2.01(1) N 2.142(7) dmsoS 2.204(2) Cl 2.413(2) not given		μC,N 81.3(4)[c] S,Cl 90.9(1) μC,S 95.8(3) N,S 176.0(2) μC,Cl 172.0(3) not given	[112]
[{(Et_3P)$_2$(Ph)Pt}$_2$-(μ-η^1:η^5-C≡C.C_5H_4)$_2$Fe] (orange)	tr $P\bar{1}$ 2	9.073(2) 11.401(2) 14.753(3)	87.86(1) 75.60(2) 81.41(2)	$Pt^{II}C_2P_2$ FeC_{10}	PhC 2.105(2) $\mu\eta^1$C 2.031(5) Et_3P 2.293(1,7) not given		C,C 174.4(2) P,P 177.0(1) C,P 90.0(1,3.8) not given	[113]
[(Ph_3P)$_2$Pt]$_2$(μ-η^2:η^5-$O_2P(O)C_5H_4$}$_2$Fe]. MeOH (pale yellow)	tr $P\bar{1}$ 2	12.598(1) 16.388(2) 23.0691(2)	93.815(1) 104.156(1) 111.58(0)	$Pt^{II}O_2P_2$ FeC_{10}	$\mu\eta^2$O 2.092(4,6) Ph_3P 2.252(2,10) not given		O,O 70.7(1,1)[g] P,P 100.13(6,22) O,P 94.5(1,3.6) not given	[114]
[{(Et_3P)$_2$(Ph)Pt}$_2$-(μ-η^2:η^5-$C_{23}H_{11}$).Fe(η^5-cp)] (red)	tr $P\bar{1}$ 2	12.298(1) 13.810(1) 18.768(1)	90.42(1) 94.56(1) 91.92(1)	$Pt^{II}C_2P_2$ FeC_{10}	PhC 2.08(1,1) $\mu\eta^2$C 2.00(1,1) Et_3P 2.286(4,12) η^5cpC 2.01(2,5) $\mu\eta^5$C 2.03(2,7)		P,P 178.4(2,8) C,P 90.0(4,3.2) not given	[115]

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Five-membered metallocyclic ring.
d. There are two crystallographically independent molecules.
e. Six-membered metallocyclic ring.
f. Three-membered metallocyclic ring.
g. Four-membered metallocyclic ring.

are three examples, [{$(H_3N)_2$Pt(μ-NHCOBu^t)$_2$}$_2$Mn] (ClO_4)$_2$.4H_2O [76], [{$(H_3N)_2$Pt(μ-η^2-meu)$_2$}$_2$Pd] (ClO_4)$_2$.2.25H_2O [80] and (NBu_4)[{$(C_6F_5)_3$Pt(μ-tht)}$_2$Ag] [85], which contain two crystallographically independent molecules that differ mostly by degree of distortion.

2.2.1.6. Pt-Pt-M linear core

There are sixteen derivatives with a Pt-Pt-M linear core. Their structural parameters are summarized in Table 3B. Structures are listed in increasing order of their Pt-M distance. In thirteen coloured derivatives, the respective complex cations (Table 3B) are composed of a Pt-Pt-M trimetalic core which is bridged by two η^3-bis(diphenylphospinomethyl)phospine-P,P',P" (dpmp) ligands. The pair of ligands creates four five-membered bimetallocycles, PtPCPPt' and Pt'PCPM (two of each) with two common edges, Pt-Pt'-M and PPt'P.

In rhe remaining three complexes [90], the Pt-Pt-Pd trimetallic core is bridged by two different η^3-L-P,P',P" ligands: η^3-dpmp and η^3-dpmpd, η^3-dpmp and η^3-dpme, and η^3-dpmp with η^3-dpmpm.

The platinum(II) as well as Pd(II) atoms are four-coordinated. The terminal xylNC ligands are the most common. The mean values of Pt-L bond distances differ between the "real" Pt center and "terminal" (satellite) Pt. The mean Pt-C(CNxyl) bond distance of 2.025 Å (range 2.01 – 2.08 Å) for the "real" Pt center is longer by 0.085 Å than that of the "terminal" Pt, with a mean value of 1.94 Å. However, for the Pt-P(η^3L) bond distances, the opposite is true, with a mean Pt-P (real center) bond

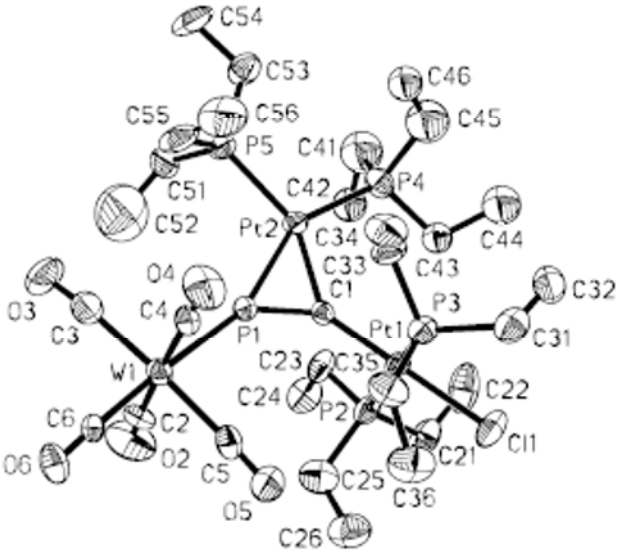

Figure 5. Structure of $(Et_3P)_4ClPt_2(\mu\text{-}C{\equiv}P)W(CO)_5$ [95].

distance of 2.280 Å (range 2.250 – 2.325 Å), which is about 0.025 Å shorter than that of the Pt-Pt (terminal) bond distance with a mean value of 2.305 Å (range 2.275 – 2.350 Å). The Pt-Pt bond distance ranges from 2.644(1) Å [92] to 2.867(2)Å [90], with a mean value of 2.698 Å.

There are six heterometal atoms, Pd (x5) [90,91], Rh (x4) [92,93], Ir (x2) [93], Cu (x3) [94], Ag (x1) and Au (x1) [94]. The shortest Pt-M bond distance is Pt-Pd with a value of 2.634(3) Å [90].

2.2.1.7. Unique structures

There are twenty four Pt_2M derivatives with variable structures that do not fit in the groups discussed above. Their structural data are summarized in Table 3C. The structure of orange Pt_2W [95] is shown in Fig. 5. As can be seen, the C≡P group, which in a unique position serves as a bridge between the metal centers, is the "real" center. Both platinum atoms are in square-planar environments (PtP_3C and PtP_2CCl). The tungsten atom has an octahedral environment (WC_5P).

The white Pt_2Ag derivative [96] is the only example that contains Pt(IV) atoms. A pair of Me_3Pt and $Ag(\eta^2\text{-tol})_2$ fragments are connected by three $\eta^2\text{-}O_2SOCF_3$ ligands. Both Pt(IV) as well as Ag(I) are pseudo-octahedrally coordinated (PtO_3C_3 and AgC_4O_2).

There are two $Pt(II)_2M(I)$ (M=Cu [97] or Ag [98]) derivatives in which two terminal (η^2-dppe)Pt in the former and two $(Ph_3P)_2Pt$ units in the latter are connected to the central M(I) by two pairs of C≡CPH groups. An M(I) cation is unsymmetrically π-bonded to all four acetylene fragments. The Pt-M distances are 3.088(5) and 3.133(5) Å in the former and 3.384(1) and 3.513(1) Å in the latter. All Pt(II) atoms are in square-planar environments (PtC_2P_2), while M(I) are tetrahedrally coordinated (MC_4).

A trinuclear asymmetric Pt_2Pd compound [99] is formed by three slightly distorted square-planar environments in $(Ph_3P)_2Pt(1)(\mu\text{-}OH)_2Pd(\mu\text{-}PPh_2)_2Pt(2)(C_6F_5)_2$. The Pt(1)...Pd distance is 3.273(1) Å and the Pt(2)...Pd distance is 3.562(1) Å, excluding the possibility of a metal-metal bond. The Pt(1)-O-Pd bridge angle of 101.4º (av.) is only 2.0º less than the Pt(2)-P-Pd angle (av. 103.3º).

The structure of the deep blue Pt_2Co derivative [100] is formed by two cis-$(\eta^2\text{-}Et_2NCS_2)Pt(POPh_2)_2$ units connected through a Co(II) cation, which is almost symmetrically bonded to all four $POPh_3$ ligands by O atoms. In another blue Pt_2Co derivative [101], two terminal fragments, $(\eta^2\text{-}Pr^i_2NCS)_2$. $Pt(POPh_3)_2$ and $(\eta^2\text{-}Pr^{iu}_2NCS)_2Pt(PSPh_2)_2$ are connected again by the Co(II) cation which is bonded to O (former fragment) and to S (latter fragment). In both derivatives, each Pt(II) atom has a distorted square-planar geometry (PtS_2P_2). Both Co/(II) atoms are tetrahedrally coordinated in CoO_4 [100] and CoO_2S_2 [101].

The structure of the yellow Pt_2Rh derivative [102] is the only example in the series of unique structures with no M atom as its "real" center. Here, two non-equivalent fragments, $(C_6F_5)_2Pt(C{\equiv}CSiMe_3)_2$ and $(\eta^5\text{-cp*})(Et_3P)Rh(C{\equiv}CSiMe_3)_2$, are connected through a platinum (II) atom. The central platinum atom is σ-bonded to two C_2 atoms of two alkynyl bridging ligands and completes its environment by η^2-coordination of the two alkyne groups of the organometallic entity "$Rh(cp^*)(C{\equiv}CSiMe_3)_2(PEt_3)$". The terminal $Pt(C_6F_5)_2$ unit is symmetrically η^2-bonded

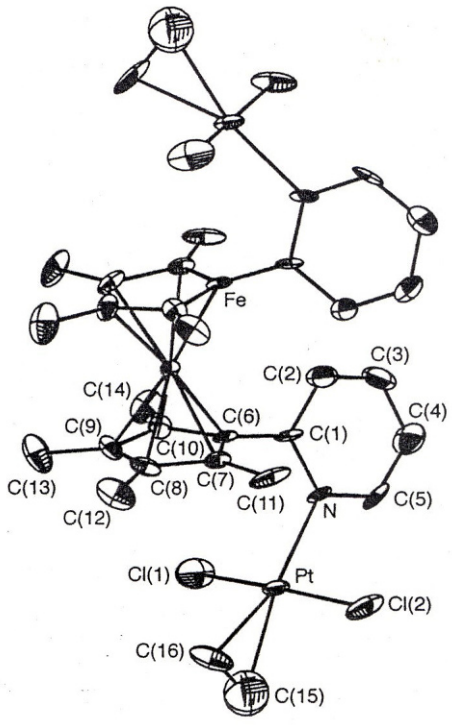

Figure 6. Structure of $[\{(\eta^2\text{-}CH_2{=}CH_2)Cl_2Pt\}_2(\mu\text{-}\eta^1{:}\eta^5\text{-}pycp^*)_2Fe]$ [109].

to the alkynyl fragments of the binuclear entity $(PEt_3)(cp^*)Rh(\mu\text{-}C{\equiv}CSiMe_3)_2Pt(C{\equiv}CSiMe_3)_2$. The Pt-Rh and Pt-Pt distances are 3.297(1) and 3.366(1) Å, respectively, excluding the possibility of metal-metal bonds.

In the blue Pt_2Cu derivative [103], two $\eta^2{:}\eta^2$-betmp-O,O',S,S' ligands serve as bridges between two (η^2-dach)Pt fragments and the Cu(II) center. All metal(II) atoms are square-planar coordinated (PtN_2S_2 and CuO_4). In the green Pt_2Cu derivative [104], two 2,2-diacetyl-1,1-ethylenedithioalate-O,O',S,S' ligands serve as bridges between two $(Ph_3P)_2Pt$ fragments and the $Cu(OClO_3)_2$ unit.

The octadentate pz(b_2:d_2) ligand serves as bridge between two $(Et_3P)_2Pt$ fragments and a nickel(II) atom [105] completes a square planar geometry about each metal(II) atom in the chromophores PtS_2P_2 and NiN_4. The Pt...Ni and Pt...Pt separations are 7.18 and 14.36 Å.

There are two Pt_2M (M=Ru [106] and Fe [107]) derivatives in which two C_5H_4 groups serve as bridges between the two (η^4-cod)ClPt [106], and (Ph_3P)(py)ClPt [107] fragments and the central M (each M is sandwiched). Each of the C_5H_4 groups is coordinated to the platinum(II) atom through one C atom. In two other (orange and green) Pt_2Fe derivatives, two platinum atoms, which are in a square-planar environment, are bridged by an OH group [107] and a thiolate ligand [108] as well as the 1,1'-ferrocenedixyl group. The Pt-X-Pt bridge angles are 138.9(2)° (X=O) and 116.8(2)° (X=S).

The structure of the red $[\{(\eta^2CH_2{=}CH_2)Cl_2Pt\}_2(\mu\text{-}\eta^1{:}\eta^5\text{-}pycp^*)_2Fe]$ [109] derivative is shown in Fig. 6. It has molecular (and crystallographic) C_2 symmetry. Each platinum atom is coordinated by one nitrogen, two chlorine and two carbon atoms. Each ethylene ligand is in an approximately perpendicular orientation to the respective Cl-Cl-N-Pt coordination plane. The dihedral angle between the plane defined by Pt,C(15) and C(16) and the best plane for Pt,Cl(1) and Cl(2) and N is 93.7°, and the relevant Cl-Pt-C-C torsion angles are close to 90°. The coordination of the two $PtCl_2(C_2H_4)$ fragments leads to pronounced angular distortions of the dpf* framework. The best planes of the cyclopentadienyl ring and the pyridyl ring attached to it intersect each other at an angle of 72.1°. The structure of another red derivative $[\{(\eta^2CH_2{=}CH_2)Cl_2Pt\}_2Cl_2Pt\}_2.(\mu\text{-}\eta^1{:}\eta^5\text{-}pycp)_2Fe]$ [110] is similar to [109].

There are two yellow and two orange Pt_2Fe derivatives [111,112] in which two $Me_2NCH_2C_5H_4$ ligands serve as bridges between two Cl_2(dmso)Pt [111], Br(dmso)Pt [111] and Cl(dmso)Pt [112] fragments and an iron center. Two Cl_2(dmso)Pt fragments are connected only through N atoms of $Me_2NCH_2C_5H_4$ and in all remaining cases, the respective fragments are connected by the N and C atoms of the C_5H_4 ring, forming five-membered metallocycles. $[\{Br(dmso)Pt\}_2(\mu\text{-}\eta^2{:}\eta^5\text{-}C_5H_4)_2Fe]$ exists in two isomeric forms [111], which differ mostly by degree of distortion.

Two $(Et_3P)_2(Ph)Pt$ fragments are connected to an iron atom by a pair of $C{\equiv}CC_5H_4$ units [113]. Each Pt(II) atom has a square-planar geometry (PtC_2P_2) and the iron atom is sandwiched (FeC_{10}). Two $\mu\text{-}\eta^2{:}\eta^5\text{-}O_2P(O)C_5H_4$ ligands serve as bridges between two $(PPh_3P)_2Pt$ fragments and the central iron atom [114]. Two O atoms from the ligands are chelated to each Pt(II) atom and create a distorted square-planar geometry with a "bite" O-Pt-O angle of 70.7° (av.). Finally, in the red Pt_2Fe derivative [115], two $(Et_3P)_2(Ph)Pt$ fragments are connected to an Fe(η^5-cp) unit by a $C{\equiv}C\text{-}C_{19}H_{11}\text{-}C{\equiv}C$ ligand. The iron atom is sandwiched and each Pt(II) atom has a square-planar geometry (PtC_2P_2).

The data in Table 3 show that there are thirteen different transition metals (the number of examples is given in parentheses): Cu (x16) > Fe (x13) > Pd (x9) > Ag (x7) > Rh (x5) > Mn (x3) ~ Ni (x3) > Co (x2) ~ Ni (x2) Au, W and Ru (each x1). The shortest Pt-M bond distance is Pt-Fe, 2.5566(15) Å [76], the shortest Pt-Pt bond distance is 2.644(1) Å [92] and the longest Pt...Pt separation is 14.36 Å [105].

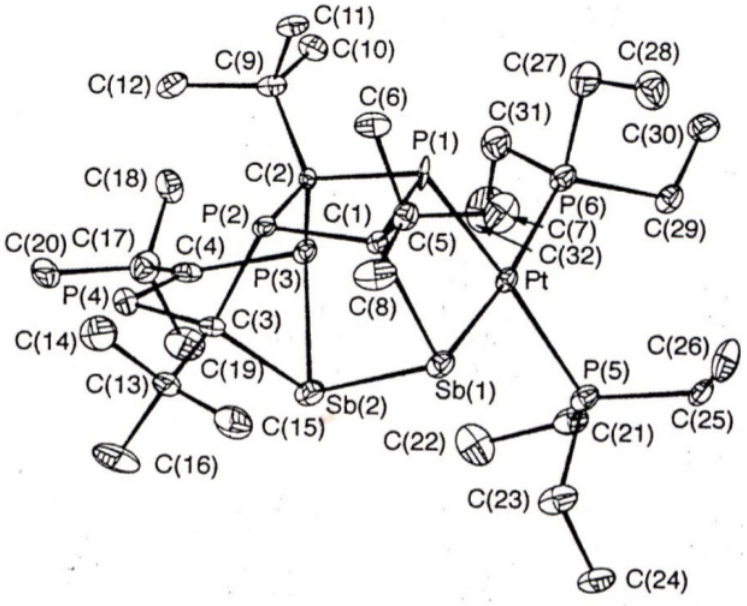

Figure 7. Structure of $[(Et_3P)_2PtSb_2(\mu\text{-}P_4C_4Bu^t_4)]$ [130].

3. PtM_2 compounds

3.1. PtM_2, M are non-transition metals

Crystallographic and structural parameters are known for forty four PtM_2 derivative (M=non-transition metal). From a structural point of view, these can be roughly divided into four categories:

- PtM_2 – asymmetrical triangular
- PtM_2 – linear
- five-, six- or seven- membered trimetallocycles
- unique structures

3.1.1. PtM_2 – asymmetrical triangular

There are twenty four examples with PtM2 asymmetrical triangular structures. Their structural data are summarized in Table 4A. This category is the richest one. The structure of the orange derivative $(Et_3P)_2Pt\{Sb(C(O)Bu^t)\}_2$ [116] is the only example with three metal-metal bonds in the respective triangular core with Pt-Sb bond distances of 2.6501(10) and 2.6667(9) Å and an Sb-Sb bond distance of 2.7551(12) Å. The Sb-Pt-Sb and Pt-Sb-Sb angles are 62.4 and 58.8º (av.), respectively.

In twenty coloured (mostly yellow) examples, in an asymmetric triangular core, only two Pt-M bonds are found, but no M-M bonds. Their structures are listed in increasing order of the sum of the two Pt-M bond distances. There are six different pairs of non-transition metals: $PtGa_2$ [117,118], $PtAl_2$ [118], $PtSn_2$ [119,121,122,125-129], $PtGe_2$ [120], $PtSb_2$ [123,124] and $PtIn_2$ [117]. The shortest Pt-M bond distances are Pt-Ga bonds in $(\eta^2dcpe)Pt\{GaC(SiMe_3)_3\}_2$ [117] with values of 2.315(1) and 2.318(1) Å. The Ga...Ga separation is 3.556 Å, which rules out a metal-metal bond. The mean Pt-M bond distance increases with the covalent radius of M, except Ga, in the order: 2.326 Å (Al, 1.18 Å) < 2.351 Å (Ga, 1.26 Å) < 2.450 Å (Ge, 1.22 Å) < 2.519 Å (Sb, 1.40 Å) < 2.545 Å (Sn, 1.41 Å) < 2.562 Å (In, 1.44 Å). The mean M-Pt-M bond angle opens in the order: 86.0º (Ge) < 91.3º (In) < 95.4º (Sn) < 97º (Sb) < 98º (Ga) < 98.7º (Al). Here, with Ge as the exception, the respective angle opens with decreasing covalent radius of M. There are three examples, $(\eta^2\text{-dhpe})Pt\{GaC(SiMe_3)_3\}_2$ [117], and $(\eta^2\text{-dhpe})Pt\{M(\eta^5\text{-cp})\}_2$, (M=Ga or Al) [118] for which quantum-chemical DFT calculations have been done, verifying rather weak Pt-M bonds for the complexes (Table 4A).

The structure of the orange $PtSb_2$ derivative [130] is shown in Fig. 7. The structure highlights a dianionic $[P_4Sb_2C_4Bu^t_4]^{2-}$ ligand chelating a distorted square-planar platinum center [P(1)-Pt-Sb(1) 76.28(6)º]. The structure contains two strained four-membered rings [P(1)-Pt-Sb(1)-C(1)]. The Pt-Sb(1)-Sb(2) angle is 82.83(3)º and the Pt-Sb(1) bond distance is 2.6152(7) Å. The Sb(1)-Sb(2) bond distance is longer by 0.153 Å (2.7681(13) Å).

The remaining two examples of this group are colourless $PtLi_2$ derivatives [131,132]. Both contain Li-Pt-Li cores, with angles of 130.3(3)º [131] and 122.5(4)º [132] which are about 37 and 30º larger than the mean M-Pt-M angles found in this group. The Pt-Li bond distances are 2.537(7) and 2.628(7) Å, respectively.

Table 4. Crystallographic and structural data for heterotrinuclear PtM_2 (M = non-transition metal) compounds[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: Asymmetry triangle								
$(Et_3P)_2Pt\{Sb.(C(O)Bu^t)\}_2$ (orange) (at 150(2) K)	m $P2_1/n$ 4	19.919(2) 16.062(4) 20.132(2)	 108.48(1) 	PtP_2Sb_2 SbCPtSb	Et_3P^b 2.283(3,3) C 2.251(12,28)	Sb 2.6501(10) 2.6667(9) Sb 2.7551(12)	P,Sb[b] not given C,Sb 99.4(3,8.6) Pt,Sb 58.79(3,29)	[116]
$(\eta^2\text{-dcpe})Pt.\{GaC(SiMe_3)_3\}_2$ (yellow orange) (at 203 K)	tr $P\bar{1}$ 2	13.569(2) 14.117(2) 16.195(2)	103.872(3) 94.823(3) 94.689(3)	PtP_2Ga GaCPt	η^2P 2.285(3,1) C 2.06(1,0)	Ga 2.315(1 2.318(1) Ga 3.556	P,P 89,08(9)[c] Ga,Ga 100.28(4) C,Pt 178.0(3,4)	[117]
$(\eta^2\text{-dhpe})Pt.\{GaC(SiH_3)_3\}_2$[d]				PtP_2Ga_2 GaCPt	η^2P 2.348 C 2.060	Ga 2.360 Ga 3.657	P,P 87.6[c] Ga,Ga 101.5 C,Pt 175.8	[117]
$(\eta^2\text{-dcpe})Pt.\{Hg(\eta^5\text{-cp*})\}_2$[e] (yellow) (at 203 K)	m $P2_1/c$ 8	12.225(9) 19.123(14) 40.55(3)	 93.889(14) 	PtP_2Al_2 AlC_5Pt PtP_2Al_2 AlC_5Pt	η^2P 2.279(2,0) η^5cp*C 2.314(7,3) η^2P 2.292(1,1) η^5cp*C 2.308(7,24	Al 2.317(2) 2.326(2) Al 3.558 Al 2.327(2) 2.335(2) Al 3.502	P,P 90.63(6)[c] Al,Al 100.02(7) not given P,P 90.38(7)[c] Al,Al 97.37(8) not given	[118]
$(\eta^2\text{-dhpe})Pt.\{Al(\eta^5\text{-cp})\}_2$[d]				PtP_2Al_2 AlC_5Pt	η^2P 2.353 η^5cpC 2.354(-,13)	Al 2.358 Al 3.659	P,P 88.8[c] Al,Al 103.2 not given	[118]
$[PPh_2(CH_2Ph)]_2.[Cl_2Pt(SnCl_3)_2]$ (yellow)	tr $P\bar{1}$ 2	12.722(3) 11.518(2) 10.674(2)	110.73(1) 79.86(2) 114.39(1)	$PtCl_2Sn_2$ $SnCl_2Pt$	Cl 2.296(2,3) Cl 2.352(2,12) 2.768(2)	Sn 2.3437(9) 2..3675(9)	Cl,Cl 101.32(8) Sn,Sn 111.48(3) Cl,Sn 73.60(6,16) Cl,Cl 98.55(7) Cl,Pt 121.38(7,3.1)	[119]
$[PMePh_3]_2.[Cl_2Pt(SnCl_3)_2]$ (yellow)	m $P2_1/n$ 2	11.815(2) 14.172(3) 13.848(2)	 96.56(1) 	$PtCl_2Sn_2$ $SnCl_3Pt$				[119]
$(\eta^2\text{-dcpe})Pt.\{Ga(\eta^5\text{-cp*})\}_2$[e] (yellow) (at 193(2) K)	m $P2_1/c$ 8	12.260(3) 18.970(5) 40.507(11)	 93.81(1) 	PtP_2Ga_2 GaC_5Pt PtP_2Ga_2 GaC_5Pt	η^2P 2.253(5,3) η^5cp*C 2.36(2,8) η^2P 2.265(5,1) η^5cp*C 2.39(2,3)	Ga 2.355(2) 2.367(2) Ga 3.538 Ga 2.371(2) 2.382(2) Ga 3.510	P,P 92.2(2)[c] Ga,Ga 97.07(7) not given P,P 92.3(2)[c] Ga,Ga 96.21(7) not given	[118]
$(\eta^2\text{-dhpe})Pt.\{Ga(\eta^5\text{-cp})\}_2$[d]				PtP_2Ga_2 GaC_5Pt	η^2P 2.3296 η^5cp 2.444(-,2)	Ga 2.439	P,P 90.5[c] Ga,Ga 99.9 not given	[118]
$(PhMe_2P)_2Pt.\{Ge(Me)(Ph)_2\}_2$ (yellow)	m $C2_1/c$ 4	15.672(5) 14.408(5) 18.012(5)	 105.891(5) 	PtP_2Ge_2 GeC_3Pt	P 2.318(2,0) MeC 1.956(8) PhC 1.990(7,14)	Ge2.4387(9,0)	P,P 97.02(11) Ge,Ge 82.56(4) P,Ge 92.86(6,0) 153.98(6,0) C,C 103.8(4,2.9) C,Pt 108.9(2,4.1) 124.7(3)	[120]
$(PhMe_2P)_2Pt.\{Ge(Me)_2Ph\}_2$ (yellow)	m C2/c 4	17.417(1) 11.430(1) 17.424(1)	 108.895(5) 	PtP_2Ge_2 GeC_3Pt	P 2.334(2,0) MeC 1.990(9,3) PhC 1.973(9)	Ge 2.4345(9) 2.4455(9)	P,P 94.29(10) Ge,Ge 85.15(4) P,Ge 92.27(6,1) 164.14(6,1) C,C 102.3(3,5.9) C,Pt 111.8 (2) 117.8(2,2)	[120]
$(\eta^2\text{-dmpe})Pt.\{Ge(Me)Ph_2\}_2$ (yellow)	m $P2_1/n$ 4	10.686(1) 18.669(1) 17.660(1)	 105.581(2) 	PtP_2Ge_2 GeC_3Pt_2	η^2P 2.300(2,2) MeC 1.976(8,2) PhC 1.972(7,20)	Ge 2.454(1) 2.455(1)	P,P 85.1(1)[f] Ge,Ge 86.7(1) P,Ge 94.4(1,7) 173.8(1,5) C,C 103.2(3,4.2) C,Pt 115.1(3,4.9)	[120]
$[(\eta^2\text{-dppe})Pt.\{Ge(Me)Ph_2\}_2].C_6H_6$ (yellow)	m $P2_1/n$ 4	15.754(2) 19.864(2) 17.025(2)	 105.401(9) 	PtP_2Ge_2 GeC_3Pt	η^2P 2.307(3,13) MeC 1.974(12,20) PhC 1.998(7,9)	Ge 2.4616(12) 2.4729(12)	P,P 85.2(1)[f] Ge,Ge 85.18(4) P,Ge 94.99(8,25) 175.03(8,1.43) C,C 103.1(5,5.9) C,Pt 109.0(2,2.1) 118.5(4,1.6)	[120]

Continued **Table 4.** Crystallographic and structural data for heterotrinuclear PtM_2 (M = non-transition metal) compounds[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(NEt_4)_2[Cl_2Pt.(SnCl_3)_2]$ (yellow)	m $P2_1/n$ 4	12.148(1) 13.667(1) 19.340(2)	 90.42(1) 	$PtCl_2Sn_2$ $SnCl_3Pt$	Cl 2.350(5,6) Cl 2.348(5,18)	Sn 2.484(1) 2.495(1)	Cl,Cl 91.5(1) Sn,Sn 97.8(1) Cl,Sn 85.4(1,20) Cl,Cl 97.5(2,2.0) Cl,Pt 149.7(1,5.3)	[121]
$[PPh_3Me]_2[Br_2Pt(SnBr_3)_2]$ (orange)	tr $P\bar{1}$ 3	12.293(6) 12.868(6) 25.047(8)	96.11(3) 91.06(3) 116.53(3)	$PtBr_2Sn_2$ $SnBr_3Pt$	Br 2.453(3,6) Br 2.512(4,15)	Sn 2.488(2) 2.503(2)	Br,Br 90.6(1) Sn,Sn 96.1(1) Br,Sn 86.7(1,3) 175.7(1,1.3) Br,Br 98.1(1,4.0) Br,Pt 119.3(1,4.2)	[122]
$Cl_2Pt\{Sb(Ph)_3\}_2$[e] (yellow)	m $P2_1/a$ 8	20.5708(12) 10.1942(4) 33.3984(15)	 94.394(4) 	$PtCl_2Sb_2$ SbC_3Pt $PtCl_2Sb_2$ SbC_3Pt	Cl 2.325(4,1) C not given Cl 2.335(4,2) C not given	Sb 2.491(1) 2.510(1) Sb 2.497(1) 2.512(1)	not given not given 	[123]
$Br_2Pt\{Sb(Ph)_3\}_2$ (yellow)	m $P2_1/c$ 4	33.779(4) 9.938(2) 20.543(5)	 95.92(3) 	$PtBr_2Sb_2$ SbC_3Pt	Br 2.456(2,14) C 2.138(2)	Sb 2.497(1) 2.513(1)	Sb,Sb 97.1(1) Br,Sb 85.6(1,2.0) 174.9(1,1.4) not given	[124]
$I_2Pt\{Sb(Ph)_3\}_2$ (red)	m $P2_1/c$ 4	18.108(4) 10.102(2) 19.115(5)	 95.241(16) 	PtI_2Sb SbC_3Pt	I 2.602(1,5) C not given	Sb 2.550(1) 2.554(1)	not given 	[123]
$(Ph_3P)_2Pt_2.\{Sn)\eta^2\text{-acac})_2\}_2$ (orange)	or $Pca2_1$ 4	19.327(5) 12.811(2) 21.978(2)	 	$Pt^0P_2Sn_2$ SnO_4Pt	P 2.261(4) η^2O not given	Sn 2.558(1,0)	P,P 120.1 	[125]
$(\eta^2\text{-dcpe})Pt.\{In(\eta^5\text{-cp*})\}_2$ (ocre) (at 203 K)	m $P2_1/c$ 4	12.366(2) 20.27(4) 20.211(4)	 106.629(5) 	$Pt^0P_2In_2$ InC_5Pt	η^2P 2.244(2,3) η^5cp*C 2.578(6,27	In 2.556(1) 2.569(1) In 3.666	P,P 93.22(6)[c] In,In 91.34(2) P,In 118.69(4,1.93) not given	[117]
$(\eta^2\text{-dhpe})Pt.\{In(\eta^5\text{-cp})\}_2$[e] (ocre)				PtP_2In_2 InC_5Pt	η^2P 2.317 η^5cpC 2.615(-,7)	In 2.600 In 3.916	P,P 91.0[c] In,In 97.7 P,In 119.3 not given	[117]
$[NBu_3Me]_2.[(\eta^2\text{-dppp})Pt.\{Sn(\eta^5\text{-}B_{11}H_{11})\}_2]$ (yellow green)	or Pbcn 4	20.2351(6) 19.5630(7) 17.9094(7)	 	PtP_2Sn_2 SnB_5Pt	η^2P 2.279(2) η^2B 2.300(8,22)	Sn 2.596(1,0)	P,P 91.07(8)[c] Sn,Sn 88.87(2) P,Sn 91.32(4) not given	[126]
$[Pt\{(\mu\text{-}\eta^2\text{-}Ph_2P.CH_2CH_2)Sn.(Me)_2\}_2$ (colourless)	m $P2_1/n$ 4	11.801(2) 13.206(3) 21.697(4)	 103.144(15) 	$Pt^{II}P_2Sn_2$ SnC_3Pt	$\mu\eta^2$P 2.284(1,2) MeC not given	Sn 2.5973(5) 2.6047(5)	not given 	[127]
$[(Et_3P)_2Pt.\{Sn((Me)_3\}_2$ (yellow) (at 137 K)	m C2/c 4	19.369(7) 13.645(5) 18.056(3)	 98.83(2) 	PtP_2Sn_2 SnC_3Pt	P 2.299(1) MeC not given	Sn 2.6289(6,0)	P,P 104.23(6) Sn,Sn 82.91(2) 	[128]
$(Et_3P)_2Pt.\{Sn(\eta^5\text{-}B_{11}H_{11})\}_2$ (yellow)	m C2/c 4	30.573(4) 11.5996(14) 19.184(3)	 94.511(15) 	PtP_2CSn_2 SnB_5Pt	P 2.337(2) C 1.955(15) η^2B not given	Sn 2.640(1,0)	P,C 89.07(5) P,Sn 92.34(5) C,Sn 120.3(1)	[129]
$[(Et_3P)_2Pt.Sb_2.(\mu\text{-}P_4C_4Bu^t_4)].CH_2Cl_2$ (orange)	m $P2_1/n$ 4	10.693(4) 18.842(2) 22.7370(8)	 102.15(2) 	$Pt^{II}P_3Sb$ SbCPtSb SbCPtSb	Et_3P 2.323(2,8) P 2.434(2) C 2.242(8) C 2.225(8) P 2.515(3)	Sb 2.6152(7) Sb 2.768(1)	P,P 95.19(8,3.9) 168.79(8) P,Sb 78.28(8) 92.92(6) 166.10(7) C,Pt 87.6(2) C,Sb 89.5(2) Pt,Sb 82.83(3) C,P 80.1(2) C,Sb 93.6(3) P,Sb 101.03(7)	[130]

Continued **Table 4.** Crystallographic and structural data for heterotrinuclear PtM_2 (M = non-transition metal) compounds[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$Pt\{\mu$-η^2:η^2-CH_2.$(CMe_2)_2CH_2\}_2\{Li.(\eta^2$-tmen$)\}_2$ (colourless) (at 183 K).	m C2/c 4	14.668(1) 15.783(2) 14.814(1)	 92.75(1) 	$Pt^{II}C_4Li_2$ LiN_2C_2Pt	μC 2.124(4,2) η^2N 2.139(8,42) μC 2.176(8) 2.278(9)	Li 2.537(7) C 71.3(2,1.0)	μC,μC 80.8(2)[f] Li,Li 130.3(3) μC,μC 92.6(3) μC,Pt 52.4(2,5)	[131]
$Pt\{\mu$-η^2:η^2-$(CH_2)_4\}_2$.$\{Li(\eta^3$-pmdeta$)\}_2$ (colourless)	m C2 2	18.235(5) 9.031(1) 9.959(4)	 91.72(1) 	$Pt^{II}C_4Li_2$ LiN_3C_2Pt	μC 2.120(4,1) η^3N 2.258(9,30) 2.371(9) μC 2.691(10,57)	Li 2.628(7) C 64.9(2,1.2)	μC,μC 83.0(2,2)[f] Li,Li 122.5(4) N,N 79.4(3,1.2)[f] 115.3(4) μC,μC 67.5(2)	[132]
B: M – Pt - M LINEAR								
$Pt_2(\mu$-η^2:η^2-$(CH_2)_4\}_2$.$\{Li(\eta^2$-tmen$)\}_2$ (colourless) (yellow orange)	tr P$\bar{1}$ 3	7.799(5) 8.673(8) 10.264(6)	79.59(5) 86.89(5) 69.86(5)	$Pt^{II}C_4Li_2$ LiN_2C_2Pt	μC 2.127(4,14) η^2N 2.118(8,8) μC 2.378(8,77)	Li 2.453(7) C 66.9(2)	μC,μC 81.8(2)[f] Li,Li 180 N,Pt 112.6(3) 161.6(4)	[133]
$(PhMe_3P)_2Pt.\{Ge(Ph)_3\}_2$ (yellow)	m $P2_1/c$ 4	16.4320(5) 11.2320(2) 25.4170(6)	 105.918(1) 	$Pt^{II}P_2Ge_2$ $Ge^{II}C_3Pt$	P 2.306(1,6) PhC 1.993(4,6)	Ge 2.520(3) 2.5239(4)	P,P 173.17(3) Ge,Ge 175.075(12) P,Ge 90.14(2,2.63) C,C 101.94(14,3.03) C,Pt 110.2(2,2.1) 120.49(9)	[120]
$(Br)(Ph)Pt.\{Sb(Ph)_3\}_2$ (yellow)	m $P2_1/c$ 4	16.775(3) 11.126(2) 20.651(4)	 96.15(2) 	$Pt^{II}CBrSb_2$ $Sb^{III}C_3Pt$	PhC 1.990(2) Br 2.496(2) PhC 1.125(1)	Sb 2.548(1)	C,Sb 86.8(1) Br,Sb 90.0(1,3.2) Sb,Sb 173.6(1) not given	[124]
$\{(PhO)_3P\}_2Pt.(SnCl_3)_2$ (yellow)	m $P2_1/n$ 2	11.177(1) 13.181(2) 14.489(3)	 98.52(1) 	$Pt^{II}P_2Sn_2$ $Sn^{II}Cl_3Pt$	P 2.272(3) Cl 2.342(6,10)	Sn 2.599(2)	P,P 180.0 Sn,Sn 180.0 P,Sn 91.3(1) Cl,Cl 99.5(2,3.1) Cl,Pt 118.2(1,3.3)	[134]
$[(\eta^2$-$Bu^t_2bpy)(Me)_2.PtSn(Me)_2.(\mu$-$S)_2Sn(Me)_2].Me_2CO$ (yellow)	m $P2_1/n$ 4	14.597(3) 13.196(3) 18.975(3)	 104.41(1) 	$Pt^{IV}N_2C_2SSn$ $Sn^{II}C_2SPt$ $Sn^{II}C_2S_2$	η^2N 2.17(1,3) MeC 2.07(1,2) μS 2.439(3) MeC not given μS 2.435(4) MeC not given μS 2.385(3,31)	Sn 2.552(1) S 108.2(1) S 100.1(1)	μS,Sn 92.74(9) μS,Pt 110.6(1) μS,μS 108.9(1)	[135]
$(\eta^2$-$Bu^t_2bpy)(Me)_2.PtSn(Ph)_2(\mu$-$S)_2.Sn(Ph)_2$ (yellow)	m $P2_1/c$ 4	12.305(1) 16.667(1) 20.999(2)	 92.58(1) 	$Pt^{IV}C_2N_2SSn$ $Sn^{II}C_2SPt$ $Sn^{II}C_2S_2$	MeC 2.075(8,6) η^2N 2.167(6,25) μS 2.457(2) PhC not given μS 2.425(3) PhC not given μS 2.379(3,27)	Sn 2.558(1) S 107.76(9) S 98.03(9)	μS,Sn 90.06(6) μS,Pt 112.38(6) μS,μS 109.73(9)	[136]
$(\eta^2$- $Bu^t_2bpy)(Me)_2 PtSn(Ph)_2(\mu$-$Se)_2.Sn(Ph)_2$ (yellow)	m $P2_1/c$ 4	12.372(1) 16.702(2) 21.113(7)	 90.26(2) 	$Pt^{IV}C_2N_2$. SeSn $Sn^{II}C_2SePt$ $Sn^{II}C_2Se_2$	MeC 2.07(1,2) η^2N 2.160(8,26) μSe 2.570(1) PhC not given μSe 2.556(2) PhC not given μSe 2.506(2,22)	Sn 2.566(1) Se 105.56(5) Se 95.22(5)	μSe,Sn 89.97(4) μSe,Pt 114.32(4) μSe,μSe 110.22(5)	[136]
$(\eta^2$-$Bu^t_2bpy)(Me)_2.PtSn(Ph)_2(\mu$-$Te)_2.Sn(Ph)_2$ (yellow)	m $P2_1/c$ 4	12.481(3) 16.848(4) 21.204(5)	 92.05(2) 	$Pt^{IV}C_2N_2$. TeSn $Sn^{II}C_2TePt$ $Sn^{II}C_2Te_2$	MeC 2.07(2,1) η^2N 2.16(1,3) μTe 2.719(1) PhC not given μTe 2.700(2) PhC not given μTe 2.690(2,10)	Sn 2.571(1) Te 102.79(4) Te 91.65(6)	μTe,Sn 89.51(4) μTe,Pt 117.63(5) μTe,μTe 110.47(6)	[136]
$(\eta^2$-$Bu^t_2bpy)(Me)_2.PtSn(Me)_2\{\mu$-$\eta^2$-SeC.$(CO_2Me)$=C.$(CO_2Me)\}.(\mu$-Se$)Sn(Me)_2$ (yellow)	tr P$\bar{1}$ 2	10.8110(3) 12.5192(2) 15.0604(3)	73.895(1) 70.862(1) 86.729(1)	$Pt^{IV}C_2N_2$ SeSn $Sn^{II}C_2SePt$ $Sn^{II}C_3Se$	MeC 2.075(5,10,2) η^2N 2.192(4,36) $\mu\eta^2$Se 2.5380(5) MeC not given μSe 2.5671(6) MeC not given $\mu\eta^2$C 2.161(6) μSe 2.5137(6)	Sn 2.5625(4)	Se,Sn 84.12(1) μSe,Pt 114.52(2) C,μSe 112.4(1)	[137]

Continued **Table 4.** Crystallographic and structural data for heterotrinuclear PtM_2 (M = non-transition metal) compounds[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [º] ß [º] γ [º]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [º]	L – M - L [º]	Ref
$(Ph_3P)_2PtSn.$ $(\eta^1\text{-tfmp})_2(\mu\text{-O})_2.$ $Sn(\eta^1\text{-tfmp})_2$ (yellow)	tr P$\bar{1}$ 2	14.458(12) 17.739(15) 19.40(2)	67.93(6) 73.62(7) 79.35(7)	$Pt^{II}P_2OSn$	P 2.234(3) 2.353(3) μO 2.047(5)	Sn 2.628(1)	P,P 97.16(10) P,μO 78.4(2) 175.2(2) μO,Sn 85.7(2)	[138]
				$Sn^{II}C_2OPt$	η^1C 2.262(9,5) μO 2.005(6)		C,C 102.6(3) C,μO 106.7(3)	
				$Sn^{II}C_2O_2$	η^1C 2.223(9,10) μO 1.934(6,6)		C,C 101.4(3) μO,μO 101.0(3)	
D: UNIQUE STRUCTURES								
$(PhMe_2P)_2PtGe.$ $(Ph)_2(Me)\{\mu\text{-}\eta^2\text{-C(Ph).}$ $=CH)Ge(Ph)_2(Me)$ (yellow) (at 120 K)	tr P$\bar{1}$ 2	11.349(2) 11.515(2) 20.271(3)	98.370(7) 98.342(7) 115.056(8)	Pt^0P_2CGe	P 2.334(3,19) $\mu\eta^2$C 2.108(9)	Ge 2.4682(11)	P,P 94.99(10) P,C 88.3(3) 175.8(3) P,Ge 92.69(7) 171.04(7) C,Ge 84.2(3)	[120]
				$Ge^{IV}C_3Pt$	MeC not given PhC not given		C,C 103.7(5,2.4) C,Pt 114.8(4,4.9)	
				$Ge^{IV}C_4$	MeC 1.976(12) PhC 1.968(12) $\mu\eta^2$C 1.927(10)		C,C 109.6(5,6.8)	
$(Me)PtSn(Me)_2.$ $\{\mu\text{-}\eta^2\text{-}CH_2CH_2PPh_2\}_2.$ $Sn(Me)_3$ (colourless)	tr P$\bar{1}$ 2	12.4142(1) 12.8091(2) 15.7898(3)	66.396(1) 69.796(1) 66.749(1)	Pt^0P_2CSn	$\mu\eta^2$P 2.274(3) 2.327(3) MeC 2.137(11)	Sn 2.5936(8)	P,P 104.30(9) P,C 87.8(3) 167.4(3) P,Sn 82.55(7) 173.13(7) C,Sn 85.3(3)	[139]
				$Sn^{IV}C_3Pt$	MeC 2.140(12,10) $\mu\eta^2$C 2.137(11)		C,Pt 116.9(4,1.3) μC,Pt 102.5(3)	
				$Sn^{IV}C_4$	MeC not given μC 2.131(10)		not given	
$[Cl_2Pt\{(\mu\text{-}\eta^2\text{-}Ph_2P.$ $CH_2CH_2)Sn(Me)_2.$ $(Cl)\}_2]$ (colourless)	m P2/c 8	36.806(6) 10.313(2) 20.320(3)	 102.24(2) 	$Pt^{II}Cl_2P_2$	Cl 2.371(1,7) $\mu\eta^2$P 2.259(1,7)		Cl,Cl 87.0(1) P,P 99.1(1) Cl,P 87.2(1,2.1) 171.7(1,3.3)	[140]
				$Sn^{IV}C_3Cl$	MeC 2.125(4,13) $\mu\eta^2$C 2.143(4,0) Cl 2.459(1,41)		C,C 118.3(2,10.4) C,Cl 96.7(1,6.7)	
$Pt\{(\mu\text{-}\eta^2\text{:}\eta^2\text{-dmg}).$ $Ga(Me)_2\}_2$ (yellow)	tr P$\bar{1}$ 2	6.185(1) 7.517(2) 10.307(2)	92.9(1) 102.9(1) 90.1(1)	$Pt^{II}N_4$	η^2N 1.988(17,0) 2.031(9)		N,N 77.2(3)[f] 102.8(3)[c] 180.0(3)	[141]
				$Ga^{III}O_2C_2$	$\mu\eta^2$O 1.924(13,10) MeC 1.968(22,14)		O,O 97.5(3) C,C 128.2(4) O,C 106.7(4,4.0)	
$[NEt_4]_2[Pt\{\mu\text{-Cl})_2.$ $HgCl_2\}_2]$ (yellow)	m $P2_1/c$ 2	10.43(2) 9.80(2) 15.12(3)	 91.0(1) 	$Pt^{II}Cl_4$	μCl 2.29 2.32		not given	[142]
				$Hg^{II}Cl_4$	Cl 2.31(-,1) μCl 2.83(-,10)		Cl,Cl 148	
$[NEt_4][Pt\{\mu\text{-Cl})_2.$ $HgCl_2\}_2][HgCl_2]$ (yellow)	tg $P4_2/mnc$ 2	8.71(2) 22.81(5)	 	$Pt^{II}Cl_4$ $Hg^{II}Cl_4$ (x2) $HgCl_2$	μCl 2.32 Cl 2.33 μCl 2.86 Cl 2.26		not given Cl,Cl 156 not given	[142]
$[Pt\{(\mu\text{-}\eta^2\text{:}\eta^2\text{-mtp})_2.$ $Hg\}_2](PF_6)_2.$ $0.5C_2H_4Cl_2.$ (yellow)	tr P$\bar{1}$ 2	11.264(9) 13.666(3) 20.930(5)	107.965(1) 94.548(1) 94.848(1)	$Pt^{II}S_4$	η^2S 2.338(4,13)	Hg 3.138(1)	S,S 178.7(1) Hg,Hg 149.1(1)	[143]
				$Hg^{II}C_2$	$\mu\eta^2$C 2.09(1,2)		C,C 173.0(4)	
$(NBu_4)_2[Pt(\mu\text{-}\eta^2\text{:}\eta^4\text{-}$ $obet)_2(HgCl_2)_2]$ (yellow) (at 139 K)	or Pbca 4	18.300(5) 18.692(4) 18.987(5)	 	$Pt^{II}C_4$ $Hg^{II}C_4Cl_2$	μC not given μC 2.53(2,1) C 2.73(2,4) Cl not given		μC,μC 90.0(7,4.2) not given	[144]
$(NBu_4)_2[Pt(\mu\text{-}\eta^2\text{:}\eta^4\text{-}$ $C\equiv CPh)_4(CdCl_2)_2].$ $0.6H_2O$ (white)	m I2/a 12	40.625(6) 20.382(1) 25.482(4)	 106.54(1) 	$Pt^{II}C_4$	μC 1.992(15,4) 2.007(13,5)	Cd 3.206(10) 3.3117(10) C 80.4(1,1.7)	not given	[145]
				$Cd^{II}C_4Cl_2$	μC 2.428(11,31) C 2.625(14,45) Cl 2.410(3,17)		not given	

Continued **Table 4.** Crystallographic and structural data for heterotrinuclear PtM_2 (M = non-transition metal) compounds[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
(η^2-cod)Pt. (μ-sqo)$_2$Tl$_2$ (pale yellow)	tr Pī 2	14.613(2) 19.703(2) 20.723(2)	98.04(4) 101.92(4) 92.99(3)	$Pt^{II}O_2C_2$ $Tl^{I}O_3$	μO 2.103(9,39) η^2C 2.10(4,6) μO 2.514(11) 2.681(11)	Tl 3.2393(15) Tl 3.7382(13)	not given not given	[146]

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. Six-membered metallocyclic ring.
d. Quantum-chemical DFT calculations
e.There are two crystallographically independent molecules.
f. Five-membered metallocyclic ring.

There are two examples, (η^2-dcpe)Pt{M(η^5-cp*)}$_2$ (M=Al or Ga) [118] which contain two crystallographically independent molecules, that differ mostly by degree of distortion.

3.1.2. PtM_2 – linear array

There are four PtM_2 derivatives which contain a linear array of MPtM. Their structural parameters are gathered in Table 4B. X-ray analysis of the colourless $PtLi_2$ derivative shows [133] that the three metal atoms form a linear Li-Pt-Li array with two equal Pt-Li bond distances of 2.453(7) Å. There are two $CH_2CH_2CH_2CH_2$ ligands, which bridge the linear Li-P-Li array forming a pair of "central" five-membered rings with a common Pt atom (PtCCCC). In addition, there are "terminal pairs" of three-membered rings (LiCPt) with common LiPt edges.

In the yellow $PtGe_2$ derivative [120], an almost linear Ge-Pt-Ge array (175.075(12)º) with Pt-Ge bond distances of 2.5207(3) and 2.5239(4) Å is found. Three phenyl groups around each Ge(II) atom complete a tetrahedral geometry (GeC_3Pt) and two PMe_2Ph ligands around the Pt(II) center complete a square-planar geometry (PtP_2Ge_2).

In yellow (Br)(Ph)Pt{Sb(Ph)$_3$}$_2$ [124], the Pt-Sb bond distances are equal to 2.548(1) Å in the Sb-Pt-Sb array, with an angle of 173.6(1)º. All metal atoms are four-coordinated, $Pt(II)CBrSb_2$ with a square-planar geometry and $Sb(II)C_3Pt$ with a tetrahedral geometry.

Four-coordinated metal(II) atoms are found in yellow derivative [134]: PtP_2Sn_2 (square-planar) and two $SnCl_3Pt$ (tetrahedral), with a linear Sn-Pt-Sn array with equal Pt-Sn bond distances, 2.599(2) Å.

3.1.3. Five-membered PtESnESn ring

There are five yellow examples which contain five-membered {PtSnESnE} (E=O,S,Se or Te) rings and also one yellow example with a seven-membered PtSnSeSnCCSe ring. Their structural parameters are summarized in Table 4C. The structures are listed in order of increasing Pt-Sn bond length.

Four derivatives with formula [(η^2-Bu$^t_2$bpy)(Me)$_2$PtSn(Me)$_2$(μ-E)Sn(Me)$_2$] E=S [135,136], Se or Te [136] are isostructural. The five-membered (PtSnESnE) metallocycles adopt an envelope conformation with the platinum(IV) atom in the "flap" position, but the fold angle follows the sequence E: Te(34º) > Se(32º) > S(30º). Within the five-membered ring, the Sn(1)-E(1)-Sn(2) angle is substantially less than the Sn(2)-E(2)-Pt angle and follows the series (E): S (99.1º (av.) and 107.9º (av.)) > Se (95.22(5)º and 105.56(5)º) > Te (91.65(6)º and 102.79(4)º). The Pt-Sn(1)-E(1) angle varies markedly as E=Te (117.63(2)º) > Se (114.32(9)º) > S (111.5º (av.)). The Pt-Sn(1) bond distance increases in the sequence E=S (2.555 Å (av.) < Se (2.566(1) Å) < Te (2.571(1) Å). Each Pt(IV) atom has a pseudo-octahedral arrangement (PtN_2C_2ESn). The Sn(IV) atoms are tetrahedrally coordinated with the chromophores $Sn(1)C_2EPt$ and $Sn(2)C_2S_2$, respectively.

X-ray analysis of (η^2-Bu$^t_2$bpy)(Me)$_2$PtSn(Me)$_2${μ-SeC(CO$_2$Me) = C(CO$_2$Me)(μ-SeSn. (Me)$_2$ shows [137] thattheseven-membered{PtSn(2)Se(2)Sn(1)C=CSE(1)} ring which forms has a twisted conformation, and this leads to relatively short transannular distances: 3.42 Å for Sn(2)...Se(1) and 3.48 Å for Sn(1)...Se(1). The Pt-Sn(2) bond distance is 2.5625(4) Å. The Pt(IV) atom has a pseudo-octahedral coordination (PtN_2C_2SeSn) and Sn(II) atoms a have a tetrahedral coordination (Sn(2) C_2SePt and Sn(1)C_3Se).

In the remaining yellow $PtSn_2$ derivative [138], a five-membered PtSnOSnO ring is found with a Pt-Sn bond distance of 2.628(1) Å, which is the longest in this series (Table 4C). Unfortunately, the original paper lacks angles within the five-membered ring and therefore it cannot be compared with similar PtSnESnE rings [135,136].

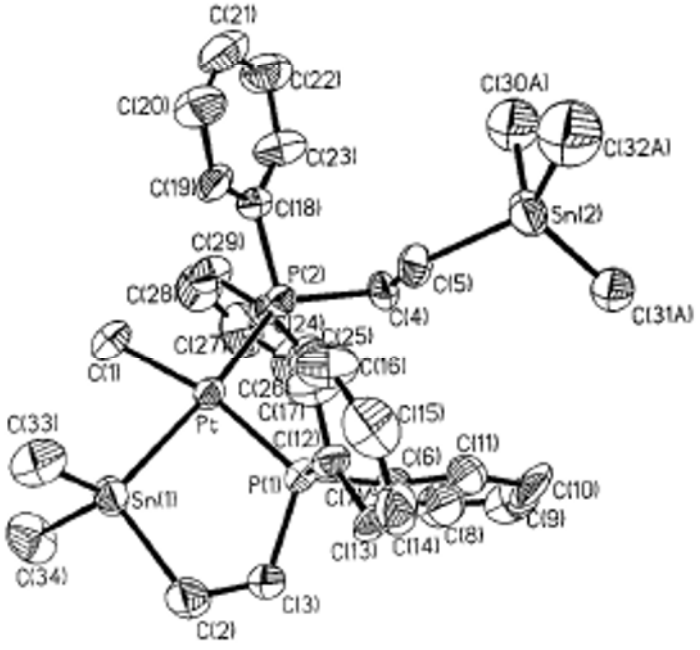

Figure 8. Structure of $[MePtSn(Me)_2(\mu\text{-}\eta^2\text{-}CH_2CH_2PPh_2)_2Sn(Me)_3]$ [139].

3.1.4. Unique structures

There are ten PtM_2 (M=non-transition metal) derivatives with unique structures. Their structural parameters are gathered in Table 4D. In the yellow $PtGe_2$ derivative [120], the cis-$(PhMe_2P)Pt$ fragment is directly bonded to the $Ge(Ph)_2(Me)$ fragment (Pt-Ge, 2.4682(11) Å) and to the $CH{=}C(Ph)Ge(Ph)_2Me$ fragment (Pt-C(H), 2.108(9) Å). The platinum(0) has a square planar arrangement (PtP_2CGe). Each Ge(IV) atom has a tetrahedral environment, GeC_3Pt and GeC_4, respectively.

The structure of the colourless $PtSn_2$ derivative [139] is shown in Fig. 8. The cis arrangement is composed of the two phosphorus ligands with one dangling phosphanylalkylstannane. The Pt-Sn(1) bond distance of 2.5936(8) Å is about 0.125 Å longer than found in [120]. The stereochemistry about each metal center is similar to those found in [120].

In another colourless $PtSn_2$ derivative [140], the central Pt(II) atom is connected to two terminal $Sn(Me)_2Cl$ fragments by a pair of $Ph_2PCH_2CH_2$ ligands with a mean Pt-P bond distance of 2.259 Å. Each Sn(IV) atom is connected by a C(â) atom with equal Sn-C bond distances of 2.143(4) Å. A square-planar geometry at the Pt(II) atom is completed by two chlorines ($PtCl_2P_2$). Each Sn(IV) atom has a tetrahedral arrangement (SnC_3Cl).

In the yellow $PtGa_2$ derivative [141], two dimethylglyoximate –O,N ligands serve as bridges between two terminal Me_2Ga units and the central Pt(II) atom. The central Pt(II) atom is in a distorted square-planar arrangement (PtN_4) with two five-membered rings (N-Pt-N, 77.2º) in a "bite" conformation. In addition, there is a pair of six-membered bimetallic rings $\{Ga(O,N)_2Pt(NO)_2Ga\}$. Both Ga(III) atoms are tetrahedrally coordinated (GaO_2C_2).

The structure of the yellow $PtHg_2$ derivative [142] contains NEt_4^+ cations and $[Pt(\mu\text{-}Cl)_2HgCl_2]_2^{2-}$ anions, well separated. The central Pt(II) atom is connected with two terminal $HgCl_2$ units by double bridged chlorine atoms as $Cl_2Hg(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2HgCl_2$. All M(II) atoms are four-coordinated: Pt is square-planar and Hg tetrahedral (MCl_4).

In the skeletal molecular structure of $[Pt\{(\mu\text{-}mtp)_2Hg\}_2]^{2+}$ [143], two mercury(II) atoms are linearly coordinated to the carbon of the mpt ligands, with the platinum(II) atom held in a distorted square-planar configuration by the four sulfur atoms. The Hg...Pt...Hg trimetallic unit is nonlinear with an angle of 149.1(1)º and the Pt...Hg separation is 3.138(1) Å. There are two eight-membered metallocycles (PtSPOHgOPS) with a common Pt atom. Each Hg(II) atom is almost linearly coordinated with a C-Hg-C angle of 173.0(4)º.

The structure of the yellow $PtHg_2$ derivative [144] consists of well separated NBu_4^+ cations and a $[Pt(\mu\text{-}obet)_2(HgCl_2)_2]^{2-}$ anion. In the double-tweezers complex anion, the Pt(II) center is in a square-planar arrangement (PtC_4) and two terminal Hg(II) atoms are tetrahedrally coordinated (HgC_2Cl_2). In the white $PtCd_2$ derivative [145], four C≡CPh ligands serve as bridges between two terminal $CdCl_2$ units and the central Pt(II) atom.

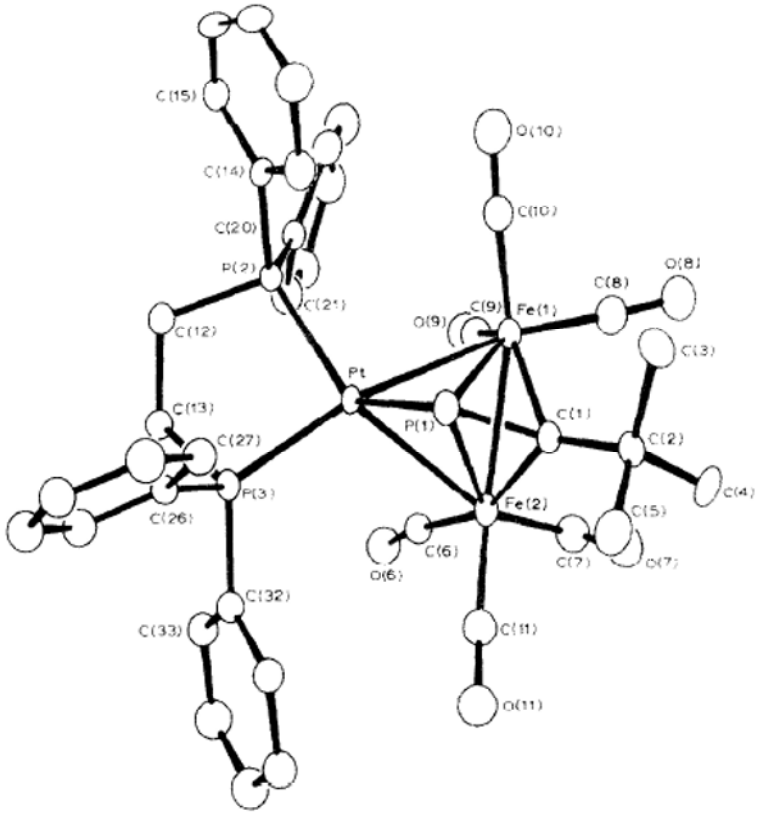

Figure 9. Structure of (η^2-dppe)$PtFe_2(\mu_3$-$PCCMe_3)(CO)_6$ [160].

Finally, there is an example [146] the structure of which consists of two silesquinoxane ligands bridged by a trinuclear (cod)$PtTl_2$ core. The metallic unit shows a Tl(1)-Tl(1) distance of 3.7382(13) Å and a Tl-Pt distance of 3.2393(15) Å. The Pt(II) atom has a square-planar geometry (PtO_2C_2). Data in Table 4 show that there are ten heterometal atoms: Sn (x17) > Ge (x6) ~ Sb (x6) > Li (x3) ~ Ga (x3) > Al (x2) ~ Hg (x2) > In, Tl and Cd (each x1). The shortest Pt-M is distance is Pt-Ge, 2.315(1) Å [117] and the shortest M-M distance is Sb-Sb, 2.7551(12) Å [116].

3.2. PtM_2 where M are transition metals

Structures of this group are complexes that can roughly be divided into several subgroups:

- PtM_2 triangular core
- PtM_2 V-shape
- $Pt(\mu_3\text{-}E)_2M_2$ E-Dicapped PtM_2 triangle
- PtM_2 linear
- double bridged
- unique structures

3.2.1. PtM_2 triangular core

There are twenty eight coloured examples in which three metal atoms form a triangle. Their structural data are gathered in Table 5A. Structures are listed in increasing order of the sum of the two Pt-M bond distances. In nine derivatives [151,153,154,156,157,161-164], all edges of the respective PtM_2 triangular core are bridged. However, in the remaining derivatives, only some edges are bridged. In three red $PtCo_2$ derivatives [147,149,150], the Co-Co edge is bridged by a carbonyl group. In the red $PtFe_2$ derivative [38], a μ-η^2-dppm ligand bridges one of the Pt-Fe edges. In another red $PtCo_2$ derivative [148], the Co-Co edge is bridged by a carbonyl group and one of the Pt-Co edges by a μ-η^2-dppa as well. Two carbonyl groups bridge the Co-Co [152] and Rh-Rh [159] edges. Both Pt-Ru edges are bridged, one by a carbonyl and another by a μ-CH_2 group. In the orange $PtIr_2$ derivative [158], each edge is bridged by μ-η^2-dppm ligand.

In the deep red $PtFe_2$ derivative [160], the C≡P fragment from the Me_3CCP ligand is stereochemically disposed above the plane of the three metal atoms (Fe(1), Fe(2), Pt) such that phosphorus P(1) is coordinated to all three metal atoms and the C(1) is bonded to the two iron atoms (Fig. 9). The phospha-alkyne-P(1) bonding distances to the three atoms (Fe(1), Fe(2), Pt) are 2.343(2), 2.446(2), and 2.343(2) Å, respectively, indicating that the P(1) atom is positioned nearly in the middle of the isosceles triangle of the three metal atoms.

Table 5. Crystallographic and structural data for heterotrinuclear PtM_2 (M is transition metal) with triangular PtM_2 core and V shape[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: PtM_2 TRIANGULAR								
(η⁴-cod)$PtCo_2$.(μ-Co)$(CO)_6$ (red brown)	or Pbca 8	15.076(3) 16.298(3) 14.547(5)		PtC_4Co_2 CoC_4PtCo	η⁴C[b] 2.20(1,3) OC 1.79(1,3) μOC 1.92(1,2)	Co 2.514(1,1) Co 2.513(2) C 60.00(4)	C,Co[b] 106.4(3,1.5) 158.2(3,3.4) Co,Co 59.96(4) μC,Pt 71.1(3,2) Pt,Co 60.02(4,2)	[147]
(OC)$PtCo_2$(μ-η²-dppa)(μ-CO)$(CO)_4$[c] (red brown)	tr P$\bar{1}$ 4	10.9719(2) 13.9234(2) 21.8041(2)	87.249(1) 83.265(1) 74.873(1)	$PtCPCo_2$ CoC_3PPtCo CoC_4PtCo	OC 1.85(2) μη²P 2.259(3) OC 1.78(2,2) μOC 1.89(1) μη²P2.175(3) OC 1.78(2,3) μOC 1.98(1)	Co 2.519(2,12) Co 2.531(2) C 81.6(5)	C,P 101,6(4) C,Co 105.5(4) 165.7(4) P,Co 92.68(9) Co,Co 60.30(5) μC,P 100.4(4) μC,Pt 69.0(4) P,Pt 94.8(1) Pt,Co 60.30(6) μC,Co 47.7(4) Pt,Co 59.40(5)	[148]
([(Ph_3)(OC)Pt.Co_2(μ-CO)$(CO)_6$].0.5tol (red brown)	m $P2_1/c$?	15.181(4) 20.334(7) 10.248(3)	108.16(1)	$PtCPCo_2$ CoC_4PtCo	not given OC 1.781(4) μOC 1.907(10,25)	Co 2.527(1,7) Co 2.507(1)	not given not given	[149]
(OC)$PtFe_2$.(μ-η²-dppm)Fe_2.$(CO)_7$ (red)	m $P2_1/n$ 2	12.128(1) 12.041(2) 23.697(4)	98.96(1)	$PtCPFe_2$ FeC_3PPtFe FeC_4PtFe	OC 1.88(1) μη²P 2.262(2) OC 1.78(1,1) μη²P 2.08(2) OC 1.77(1,2)	Fe 2.549(1,8) Fe 2.740(2)	C,Fe 100.7(3) 165.7(3) P,Fe 93.8(1) Fe,Fe 65.0(1) C,Pt 82.2(3,9.0) 157.7(4) C,Fe 92.2(4,10.6) Pt,Fe 57.8(1) C,Pt 77.6(3,5.5) 113.6;144.9(3) C,Fe 88.6(3,1.6) 170.7(3) Pt,Fe 57.2(1)	[38]
(η²-dppe)$PtCo_2$.(μ-CO)$(CO)_6$ (dark red) (at 223 K)	m $P2_1/n$ 4	13.039(3) 17.681(8) 14.614(4)	102.81(1)	PtP_2Co_2 CoC_4PtCo	η²P 2.234(1,0) OC 1.781(7,21) μOC 1.925(5,27)	Co 2.5407(7) 2.5589(7) Co 2.533(2)	P,P 86.40(5) P,Co 107.09(5,83) Co,Co 59.55(2) Pt,Co 60.22(2,36)	[150]
(η⁴-cod)pTfE_2.$(CO)_8$ (deep red)	or $P2_12_12_1$ 4	12.321(11) 9.442(7) 15.707(16)		PtC_4Fe_2 FeC_4PtFe	η⁴C 2.23(2,3) OC 1.80(2,4)	Fe 2.557(3,4) Fe 2.704(4)	C,C 34.1(7,4)[d] Fe,Fe 63.83(8) Pt,Fe 58.08(8,14)	[151]
$(Ph_3P)_2PtCo_2$.(μ-CO)$_2$(η^5-cp)$_2$ (red)	Tr P$\bar{1}$ 2	11.511(3) 12.775(3) 16.526(4)	70.46(3) 89.59(3) 64.18(2)	PtP_2Co_2 CoC_7PtCo	P 2.287(4,4) μOC 1.89(2,3) η^5cpC not given	Co 2.563(2,3) Co 2.372(2) C 77.7(6,7)	P,P 114.1(4) P,Co 95.4(1.5) not given	[152]
(Ph_3P)(OC)Pt.$Fe_2(CO)_8$ (yellow red)	m $P2_1/c$ 4	11.88(1) 14.13(2) 17.49(2)	106.9(1)	PtCPFe FeC_4PtFe	OC 1.97(3) P 2.315(8) OC 1.75(4,11)	Fe 2.530(5) 2.597(5)	C,P 97.3(7) C,Fe 92.8(7) 157.8(8) P,Fe 105.5; 169.4(2) Fe,Fe 65.1(2) Pt,Fe 57.5(1,1.2)	[153]
[$(Et_3P)_2$(Cl)Pt.$Au_2(PPh_3)_2$].CF_3SO_3 (white) (at 258 K)	tr P$\bar{1}$ 2	14.209(14) 21.938(14) 10.614(5)	81.65(6) 106.89(7) 76.57(7)	PtP_2ClAu_2 AuPPtAu	P 2.298(9) Cl 2.396(11) P 2.262(10,2)	Au 2.600(3,1) Au 2.737(3)	P,P 178.3(4) Cl,Au 148.2(3,4) Au,Au 63.5(1) P,Pt 169.1(3,4.0) P,Au 132.6(3,4.0) Pt,Au 58.2(1,0)	[154]

Continued **Table 5.** Crystallographic and structural data for heterotrinuclear PtM_2 (M is transition metal) with triangular PtM_2 core and V shape[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(Phcy_2P)PtRu_2(\mu\text{-}CH_2)(\mu\text{-}CO)Ru_2(CO)_2(\eta^5\text{-}cp)_2].0.5Et_2O$ (black)	tr P$\bar{1}$ 2	10.215(4) 12.381(4) 14.484(4)	103.54(3) 79.74(3) 85.44(3)	PtC_2PRu_2	μOC 1.94(1) μH_2C 2.05(1) P 2.288(3)	Ru 2.611(1,2) C 79.4(4,1.0)	μC,μC 166.6(5) μC,P 96.2(4,1.4) μC,Ru 51.0(3) 94.9(4) P,Ru 148.4(1) Ru,Ru 65.2(1)	[155]
				RuC_7PtRu	η^5cpC not given μOC 2.10(1) μH_2C 2.07(1)	Ru 2.813(2)	μC,μC 87.3(5,1.3) Pt,Ru 57.4(1,1)	
$(\eta^2\text{-}dppe)PtFe_2(CO)_8$ (dark green)	m C2/c 4	15.579(2) 15.654(2) 18.838(3)	105.90(2)	PtP_2Fe_2	η^2P 2.269(1)	Fe 2.612(1,0)	P,P 85.70(8)[e] P,Fe 106.31(4) Fe,Fe 62.64(4)	[156]
				FeC_4PtFe	OC 1.781(9,25)	Fe 2.716(1)	C,Pt 60.0(2) 103.6(2,16.3) 142.6(2)	
$(Et_3P)_2PtFe_2(CO)_8$ (dark red)	m C2/c 4	18.144(2) 10.843(1) 14.011(3)	101.99(2)	PtP_2Fe_2	P 2.299(2)	Fe 2.640(1,0)	P,P 105.8(1) P,Fe 97.5(1) Fe,Fe 61.4(5)	[157]
				FeC_4PtFe	OC 1.789(8,18)	Fe 2.695(2)	C,Fe 87.2(3,1.3) 175.5(3)	
$(OC)PtIr_2(\mu\text{-}\eta^2\text{-}dppm)_3(\mu\text{-}CO)(CO)_3$ (orange)	tr P$\bar{1}$ 2	13.1864(3) 13.5273(6) 17.0829(6)	76.184(2) 77.205(2) 67.111(2)	$PtCPIr_2$	OC 1.866(7) $\mu\eta^2$P 2.275(2)	Ir 2.6305(3) 2.6642(4)	C,P 102.3(3) C,Ir 102.6(3) 163.4(3) P,Ir 94.26(4) 154.85(41) Ir,Ir 60.83(1)	[158]
				IrC_2P_2PtIr	OC 1.915(9) μOC 2.065(8) $\mu\eta^2$P 2.305(2,10)	Ir 2.6810(4) C 80.8(3)	μC,Pt 70.9(2) μC,Ir 49.7(2) Pt,Ir 60.20(1)	
				IrC_3PPtIr	OC 1.896(9,19) μOC 2.071(6) $\mu\eta^2$P 2.301(2)		μC,Pt 70.0(2) μC,Ir 49.5(2) Pt,Ir 58.96(1)	
$PtIr_2(\mu\text{-}\eta^2\text{-}dppm)_3(\mu\text{-}CO)(CO)_2$ (prange)	m P2$_1$/n 4	12.905(1) 17.315(2) 32.573(3)	101.215(6)	PtP_2Ir_2	$\mu\eta^2$P 2.247(8,15)	Ir 2.628(2) 2.668(2)	P,P 109.8(3) P,Ir 1558.0(2,1.6) Ir,Ir 60.62(4)	[158]
				IrC_2P_2PtIr	OC 1.92(3,1) μOC 2.04(3,1) $\mu\eta^2$P 2.292(7,14)	Ir 2.673(2)	μC,Pt 65.3(7,4) μC,Ir 49.1(6,3) Pt,Ir 59.69(4,74)	
$(Ph_3P)(OC)Pt.Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}cp^*)_2$ (orange-brown) (at 220 K)	tr P$\bar{1}$ 2	11.185(3) 13.278(7) 15.443(9)	102.98(5) 92.18(4) 105.88(4)	$PtCPRh_2$	OC 1.83(2) P 2.285(4)	Rh 2.618(2) 2.691(2)	C,P 101.2(6) C,Rh 93.3(6) P,Rh 105.7(1) Rh,Rh 59.8(1)	[159]
				RhC_7PtRh	η^5cp*C 2.257(11,35) μOC 2.00(15,13)	Rh 2.647(2) C 82.8(5,2)	Pt,Pt 60.1(1,1.4)	
$(\eta^2\text{-}dppe)PtFe_2(\mu_3\text{-}\eta^2\text{-}PCCMe_3)(CO)_6$ (deep red)	m P2$_1$/c 4	13.238(1) 11.295(2) 25.642(2)	100.72(1)	PtP_3Fe_2	η^2P 2.267(2,4) μ_3P 2.343(2)	Fe 2.670(1,1) P 68.61(4,11)	P,P 85.10(6)[e] P,μ_3P 124.89(6,4.3) P,Fe 56.61(4,1.4)	[160]
				FeC_4PPtFe	OC 1.749(7,21) μC 2.027(6,53) μ_3P 2.394(2,63)	Fe 2.518(1) P 63.40(5) C 76.8(2)	μ_3P,Fe 111.86(4) 168.11(4) Fe,Fe 56.26(2) μ_3P,Pt 54.77(4,47) μ_3P,Fe 58.30(4,2.0) Pt,Fe 61.87(3,3)	
$(OC)_2PtOs_2(CO)_8$ (yellow)	tr P$\bar{1}$ 2	7.081(2) 9.004(2) 12.888(4)	98.46(2) 98.54(2) 74.36(2)	PtC_2Os_2	Os 2.6792,2)	Os 2.679(2,10)	not given	[161]
				OsC_4PtOs	OC 1.89(5,8)	Os 2.860(2)	not given	
$(OC)_2PtOs_2(CO)_8$ (pale yellow)	tr P$\bar{1}$ 2	8.997(3) 12.888(3) 7.082(2)	98.52 105.61(2) 81.51(2)	PtC_2Os_2	OC 1.87(2,1)	Os 2.683(1,6)	C,C 105.6(7) C,Os 95.0(5,6) 159.3(5,7)	[162]
				OsC_4PtOs	OC 1.92(2,6)	Os 2.864(1)	Os,Os 64.51(3) Pt,Os 57.74(3,19)	
$(Ph_3P)(OC)PtOs_2(CO)_7(PPh_3)$ (orange)	or Pn2$_1$a 4	16.316(9) 14.502(9) 17.605(9)		$PtCPOs_2$	OC not given P 2.40(2)	Os 2.865(3,6)	not given	[163]
				OsC_3PPtOs	not given	Os 2.916(4)	not given	
				OsC_4PtOs	not given		not given	

Continued **Table 5.** Crystallographic and structural data for heterotrinuclear PtM_2 (M is transition metal) with triangular PtM_2 core and V shape[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
(η^2-dppe)$PtRu_2$.($CO)_8$	m $P2_1/c$ 4	14.351(2) 13.486(3) 19.218(3)	 108.48(1) 	PtP_2Ru_2 RuC_4PtRu	η^2P 2.243(2.2) OC 1.90(1) 1.94(1,1)	Ru 2.7023(9) 2.7200(9) Ru 2.866(1)	P,P 86.86(8)[e] P,Ru 104.81(6,56) Ru,Ru 58.09(2,30) Pt,Ru 58.09(2,30)	[164]
[(η^2-dppe)$PtRu_2$.(μ-η^2-PtC CPh).($CO)_6$]$MeCO_2$Et.0.5C_7H_{16} (red)	or Pbca 8	23.103(2) 21.930(4) 20.663(2)	 	PtP_2CRu RuC_5PtRu	η^2P 2.292(4,16) μC 2.09(1) OC not given μC 2.03(1) 2.21(1,2)	Ru 2.684(1) 2.766(1) Ru 2.725(1)	Ru,Ru 59.99(4) Pt,Ru 60.01(4,1.49)	[165]
[$PtRu_2$(μ-η^2-dppe)$_2$.($CO)_6$].2C_6H_6 (red)	m $P2_1/c$ 4	18.836(6) 15.559(5) 23.259(7)	 111.26(2) 	PtP_2Ru_2 RuC_3PPtRu	η^2P 2.275(3,1) OC 1.87(1) $\mu\eta^2$P 2.299(3,5)	Ru 2.733(1,2) Ru 2.825(1)	P,P 101.8(1) P,Ru 98.00(9,13) 160.20(9,15) Ru,Ru 62.23(4) P,Pt 109.89(9,6) P,Ru 167.5(9,5) Pt,Ru 58.88(3,7)	[164]
[(Ph_3P)(OC)Pt.Rh_2(μ-H)(μ-CO)$_2$.(η^5-cp*)$_2$]BF_4 (red)	or Pbca 8	21.503(12) 23.728(8) 15.896(5)	 	$PtHCPRh_2$ RhC_7HPtRh RhC_7PtRh	μH 1.750(1) OC 1.96(2) P 2.297(3) η^5cp*C 2.235(11,36) μOC 2.035(11,9) μH 1.747(1) η^5cp*C 2.242(12,23) μOC 1.983(11,6)	Rh 2.705(1) 2.805(1) H 106.6(1) Rh 2.667(2) C 83.1(4,1)	C,P 99.4(4) C,Rh 84.8(4) 142.6(4) Rh,Rh 57.9(1) Pt,Rh 59.2(1) Pt,Rh 62.9(1)	[165]
(cy_3P)(OC)$PtRu_2$.(μ-H)(μ-PPh_2)($CO)_6$ (red)	m $P2_1/n$ 4	13.075(5) 20.576(4) 15.316(7)	 102.38(3) 	$PtHCPRu_2$ $RuHC_3PPt.Ru$ RuC_3PPtRu	μH 1.65(4) OC 1.847(7) P 2.332(2) μH 1.66(4) OC 1.906(7,23) μP 2.328(1) OC 1.900(8,37) μP 2.306(1)	Ru 2.7248(5) 2.8755(5) H 121 Ru 2.7789(6)	μH,C 170(1) μH,P 91(1) μH,Ru 30(2),88(1) C,P 98,7(2) C,Ru 82.1,140.9(2) P,Ru 119.69, 178.90(4) Ru,Ru 59.43(1) μH,Pt 30(1) μH,Ru 86(1) Pt,Ru 57.59(1) μP,Pt 78.65(4) μP,Ru 53.52(3) Pt,Ru 62.99(1)	[167]
(Ph_3P)$PtRe_2$.(μ-H)(μ-PPr_2).($CO)_8$ (yellow)	or Pbca 8	14.951(2) 18.330(2) 25.715(2)	 	PtP_2HRe_2 ReC_4HPtRe ReC_4PPtRe	Ph_3P 2.243(4) μP 2.236(5) μH not given OC 1.92(3,7) μH not given OC 1.92(3,5) μP 2.417(5)	Re 2.774(1) 2.834(1) P 74.9(2) Re 3.176(1)	P,μP 101.6(2) P,Re 145.4(1,11.6) μP,Re 55.4(1) 124.4(1) Re,Re 68.98(3) Pt,Re 56.41(2) μP,Pt 49.6(1) Pt,Re 54.61(2)	[168]
(η^4-cod)$PtRe_2$.(μ-H)$_2$($CO)_8$ (yellow)	m $P2_1$ 2	7.217(3) 17.081(5) 8.577(3)	 109.96(3) 	PtC_4HRe_2 ReC_4H_2PtRe ReC_4HPtRe	η^4C 2.19(1,1) 2.32(1,2) μH not given OC 1.96(2,4) μH not given OC 1.95(2,6) μH not given	Re 2.741(1) 2.895(1) Re 3.115(1)	Re,Re 67.03(2) Pt,Re 54.12(1) Pt,Re 58.84(1)	[169]
(Ph_3P)(OC)Pt.Re_2(μ-H)$_2$.($CO)_7$(PPh_3) (yellow)	m $P2_1/c$ 4	14.044(3) 19.343(5) 16.391(3)	 93.69(2) 	$PtHCPRe_2$ ReC_3H_2PPt Re ReC_4HPtRe	μH not given OC 1.889(10) P 2.322(2) OC 1.842(9) μH not given P 2.479(2) OC 1.951(11,33) μH not given	Re 2.788(1) 2.906(1) Re 3.203(1)	C,P 95.5(3) C,Re 78.1(3) 140.8(3) P,Re 118.06(5) 173.51(5) Re,Re 68.42(1) P,Pt 106.95(5) Pt,Re 54.04(1) Pt,Re 57.54(1)	[170]

Continued **Table 5.** Crystallographic and structural data for heterotrinuclear PtM_2 (M is transition metal) with triangular PtM_2 core and V shape[a].

COMPOUND (colour)	Crys.cl Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[$(Ph_3P)PtMn_2$. **(μ-PPh_2)$_2$$(CO)_8$]tol** **(yellow)**	tr P$\bar{1}$ 2	13.275(5) 17.718(6) 11.970(3)	97.61(2) 107.89(2) 97.74(2)	$PtPI_3Mn_2$ MnC_4PPt	Ph_3P 2.248(2) μP 2.91(2,8) OC 1.827(9,46) μP 2.300(2,10)	Mn 2.987(1) 3.082(1) P 82.7(1,1.7) Mn 3.245(2)	P,μP 102.46(9,83) μP,μP 154.33(8) Mn,Mn 64,61(4) Pt,Mn 57.69(4,1.42)	[171]
B: V – SHAPE - PtM_2								
$(Ph_3P)PtFe_2(\mu$-$CO)_2$ **(μ_3-η^2-CPmes).** **$(CO)(\eta^5$-cp$)_2$** **(black)** **(at 173 K)**	m $P2_1/c$ 4	10.234(2) 9.120(1) 38.364(10)	92.93(2)	PtC_2P_2Fe FeC_8PtFe FeC_8Fe	μOC 1.997(2) μ_3C 2.162(9) P 2.471(2) Ph_3P 2.240(2) η^5cpC not given μOC 1.915(9,36) μ_3C 1.915(9) η^5cpC not given OC 1.764(10) μOC 1.952(9) μ_3C 1.918(10)	Fe 2.577(2) C 78.0(3,2) Fe 2.518(4) C 82.1(4)	P,P 127.31(9) μ_3C,P 43.4(2)[d] 169.4(2) μ_3C.Fe 46.7(2) μ_3C,Pt 55.2(2) not given	[172]
(η^4-cod)$PtRh_2$. **(μ-η^2-$F_3CC_2CF_3$).** **(μ-CO)(η^5-cp$)_2$** **(dark red)**	m C2/c 8	27.654(5) 8.732(2) 18.622(5)	93.86	PtC_5Rh RhC_7PtRh RhC_8Rh	η^4C 2.241(8,20) μC 2.029(6) η^5cpC not given μOC 2.035(7) μC 2.035(7) η^5cpC not given μOC 2.009(7) μC 2.121(7,77)	Rh 2.628(1) 3.361(4) Rh 2.641(1) C 82.0(3)	μC,Rh 72.9(2) μC,Pt 69.8(2) μC,Rh 48.9(2) μC,Rh 49.1(2)	[173]
$(Ph_3P)(OC)Pt.$ **$Ru_2(\mu$-η^2-$C_4Bu^t)$.** **(μ-PPh_2)(μ-CO)$(CO)_6$** **(red)**	m $P2_1/n$ 4	9.2369(6) 23.055(1) 20.7034(8)	97.596(5)	PtC_2PRu RuC_4PPtRu RuC_4PRu	OC 1.905(7) μC 1.969(6) μP 2.2884(13) OC not given μC 2.266(5) μP not given OC not given C 2.151(5) μP not given	Ru 2.7725(13) C 81.46(20) Ru 2.8407(6) P 74.56(4)	C,μC 162.00(24) P,Ru 149.38(4) Pt,Ru 105.83(1) not given	[174]
(η^2-dppe)$PtRe_2$. **{μ_3-PC(CO)Bu^t}.** **$(CO)_8$** **(red)**	m $P2_1/c$ 4	14.356(4) 12.012(2) 25.570(6)	94.01(2)	PtP_3Re ReC_4PPtRe ReC_4PRe	η^2P not given μ_3P not given OC not given μ_3P 2.371(6) μ_3P 2.453(6)	Re not given Re 3.044(1)	not given not given not given	[175]

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. There are two crystallographically independent molecules.
d. Three-membered metallocyclic ring.
e. Five-membered metallocyclic ring

The phospha-alkyne-C(1) bonding distances to the two iron atoms are 1.974(6) and 2.080(6) Å.

In the $PtRu_2$ derivative [165], the PhC≡CPh ligand bridges one of the Pt-Ru edges as well as the Ru-Ru edge by its two C≡C atoms. In the red $PtRh_2$ derivative [166], one of the Pt-Rh edges is bridged by a hydride and the Rh-Rh edge is double bridged by two carbonyl groups. In the red $PtRu_2$ [167] and yellow $PtRe_2$ [168] derivatives, one of the Pt-M edges is bridged by a hydride and the M-M edge by μ-PPh_2 [167] and μ-PPr_2 [168]. There are two yellow $PtRe_2$ derivatives [169,170] in which one of the Pt-Re and Re-Re edges are bridged each by one hydride anion. In the yellow $PtMn_2$ derivative [171], two PPh_2 groups bridge both Pt-Mn edges.

In this series nine different heterometals were found that are involved in PtM_2 triangular cores. The shortest Pt-M and M-M bond distances are Pt-Co and Co-Co with values of 2.514 Å [147] and 2.372(2) Å [152], respectively. The mean Pt-M bond distance increases in the order: 2.534 Å (M=Co) < 2.600 Å (Au) < 2.602 Å (Fe) < 2.648 Å (Ir) < 2.682 Å (Os) < 2.705 Å (Rh) < 2.716 Å (Ru) < 2.823 Å (Re) < 3.034 Å (Mn). The mean M-M bond distance increases in the sequence: 2.491 Å (Co) < 2.657 Å (Rh) < 2.677 Å (Ir) < 2.688 Å (Fe) < 2.737 Å (Au) < 2.802 Å (Ru) < 2.880 Å (Os) < 3.165 Å (Re) < 3.245 Å (Mn). The mean M-Pt-M angle of 62.5° (range 56.3 – 69.0°) is about 3.8° more open

than that of M-M-Pt angles, 58.7º (range 54 - 63º). Red brown $(OC)PtCo_2(\mu\text{-}\eta^2\text{-dppa})(\mu\text{-}CO)_4$ [148] contains two crystallographically independent molecules, however only for one of them are structural data given in the original paper.

3.2.2. PtM_2 V shape

The structures of four derivatives [172-175] reveal an open V-shaped arrangement of the metal atoms with one M-M bond and only one M-Pt bond. In the black $PtFe_2$ derivative [172], the $(OC)(\eta^5\text{-cp})Fe^2(\mu\text{-CO})Fe^1(\eta^5\text{-cp})$ fragment with the Fe-Fe bond distance of 2.518(4) Å, is connected to a $Pt(PPh_3)$ unit by Fe^1(Pt-Fe(1), 2.577(2) Å. This Pt-Fe(1) edge is bridged by a carbonyl group. The mesPC ligand serves as a bridge by the C atom which connects all three metal atoms and by the P atom also to platinum. There are five different three-membered metallocycles: two pairs of PtCFe(1) (x2), Fe^1(1)CFe(2) (x2) and PtCP.

In the dark red $PtRh_2$ derivative [173], the hexafluorobut-2-yne ($F_3CC(2)C(3)CF_3$ ligand is face-bridging and is σ-bonded to Pt and Rh(1), with the C(2)-C(3) bond essentially parallel to the Pt-Rh(1) bond (2.628(1) Å), and π-bonded to Rh(2). The Rh(1)-Rh(2) bond distance is 2.641(1) Å and the Pt-Rh(2) separation is 3.361(4) Å, with the Pt-Rh(1)-Rh(2) angle opened from about 60º (in the triangle) to about 80º.

The red $PtRu_2$ derivative [174] contains the $Ru_2(\mu\text{-}PPh_2)(Cl)_6$ unit, which is connected to Pt via Ru(1) to give a bent three-metal atom chain [Pt-Ru(1)-Ru(2), 105.837(17)º, Pt-Ru(1), 2.7725(13) Å]. The $Bu^tC{\equiv}CC{=}C$ ligand is bound to all three metal atoms as a metallated alkynyl-funcionalized μ-vinylidene bridging. The Rh(1)-Rh(2) bond distance is 2.8407(6) Å.

For the last red $PtRe_2$ derivative [175] only some data are available. The $(OC)_4Re\text{-}Re(CO)_4$ unit with an Re-Re bond distance of 3.044(1) Å is connected to the $Pt(\eta^2\text{-dppe})$ unit via one Re atom to give a bent three-metal atom chain. The $Bu^tC(CO)P$ ligand is bound to all three metal atoms.

3.2.3 $Pt(\mu_3\text{-}E)_2M_2$ „E-ide bicapped PtM_2“

There are sixteen examples for which structures are viewed as E-ide bicapped heterometallic (PtM_2) triangles in a trigonal bipyramidal framework. Their structural parameters are gathered in Table 6. Structures are listed in increasing order of the M-M bond distance. There are six heterometals which are involved in this type of structure with the most common being iron (x10) [176-180,182] with two examples of manganese [183] and one example each of vanadium [181], iridium [185], ruthenium and osmium [186]. While the iron examples are red, manganese is green, vanadium is dark blue, ruthenium and osmium are orange and iridium is dark green.

In the trigonal bipyramidal framework $Pt(\mu_3\text{-}E)_2M_2$ (E=S,P,Se or Te), the Pt...M distances range from 2.91 to 3.92 Å (av. 3.3 Å). The mean M-M bond distance increases in the order of M: 2.546 Å (Fe) < 2.556 Å (V) < 2.727 Å (Mn) < 2.888 Å (Ir) < 3.2 Å (Ru,Os). Within the trigonal bipyramidal framework the mean Pt-E-M angle opens in the order of E: Te (89.8º) < Se (92.5º) < S (93º) < P (101.3º) and the M-E-M angle in the order: P (56º) < Te (61º) < Se (63.8º) < S(67º). The mean Pt-E bond distance increases in the sequence: 2.255 Å (E=P) < 2.330 Å (S) < 2.418 Å (Se) < 2.577 Å (Te).

There is one example, $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$ [176] which contains four crystallographically independent molecules that differ mostly by degree of distortion.

3.2.4 PtM_2 linear array

There are twenty eight coloured examples with M-Pt-M arrays and five examples with Pt-M-M linear or almost linear arrays. Their structural parameters are summarized in Table 7A and Table 7B. Structures are listed in inreasing order of the Pt-M distance. Crystals of two dark brown $PtCu_2$ derivatives [187] are formed by trinuclear $PtCu_2$ cations, nitrate anions and disordered water molecules. The cations are built up as head-tail-head-tail- $Pt(\mu\text{-}\eta^3\text{-mec})_4$ square-planar entities with two $Cu(OH)_2$ fragments in one and CuCl in another. This is a result of the metal centers being essentially colinear, with the Cu(II)-Pt(II)-Cu(II) angles of 179.31(10) and 178.58(3)º, respectively. The Pt-Cu bond distances are 2.519 and 2.524 Å, respectively, which are the shortest found in this group of derivatives.

There are five PtM_2 (M=Co [188], Fe [189], Mn [188], Re [198] and Mo [200]) derivatives in which all atoms (ligands) are involved as bridges. The M-Pt-M arrays are linear, with angles of 180º (M=Co,Fe,Mn and Re) and 176.93(4) Å[should this be degrees?[(M=Mo). Each of the respective derivatives contain equal Pt-M bonds, which increase in the order of M: 2.613(6) Å (M=Co) < 2.657(2) Å (Fe) < 2.743(8) Å (Mn) < 2.8309(15) Å (Re) < 2.889(2) Å (Mo).

In another three red linear Au-Pt-Au derivatives [90,190,199], four $CH_2P(S)Ph_2$ ligands bridge all three metal atoms through the S atom to Pt(II), through the C atom to Au(II) (in one example), and through the Au(I) atom in another two examples., TheAu(II)-C and Au(I)-C bond distances are 2.11 Å (av.) and 2.10 Å (av.), respectively. The mean Pt-Au bond distances are 2.665 Å (Au(II)) and 2.952 Å (Au(I)). In two monoclinic red almost linear PtW_2 derivatives, with W-Pt-W angles of 165.5(0)º [191] and 172.8(1)º [192], a pair of μ-CR (R=C_6H_4Me-4 [191]) and R=Me [192]) ligands bridge

Table 6. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with $Pt(\mu_3\text{-}E)_2M_2$ core[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(Ph_3P)_2Pt(\mu_3\text{-}S)_2\cdot Fe_2(CO)_6$[c] **(red)**	m $P2_1/c$ 16	24.885(9) 19.770(8) 34.085(12)	 90.55(1) 	$Pt^{II}S_2P_2$	μ_3S[b] 2.317(10,3) Ph_3P 2.288(9,14)	Fe 3.30 S93.8(44,2.0)	μ_3S,μ_3S[b]75.5(5) PP 92.5(3) μ_3S,P93.5(3,2.2) 169.0(3,2.2)	[176]
				$Fe^IC_3S_2Fe$	OC not given μ_3S 2.29(1,1)	Fe 2.484(7) S 65.7(3,1)	μ_3S,μ_3S 76.6(4,2) μ_3S,Fe 57.1(3,4)	
				$Pt^{II}S_2P_2$	μ_3S 2.350(9,24) Ph_3P 2.266(9,16)	S 92.1(4,1.2)	μ_3S,μ_3S 76.6(4,2) PP 97.1(4) μ_3S,P 93.1(3,1.1) 169.7(3,1.1)	
				$Fe^IC_3S_2Fe$	μ_3S 2.30(1,3) OC not given	Fe 2.494(7) S 65.8(3,3)	μ_3S,μ_3S 78.8(4,3) μ_3S,Fe 57.1(3,6)	
				$Pt^{II}S_2P_2$	μ_3S 2.34(1,3) Ph_3P 2.315(9,8)	S 92.6(4,1.5)	μ_3S,μ_3S 75.5(3) PP 98.6(3) μ_3S,P92.9(3,1.0) 168.4(3,1.1)	
				FeC_3S_2Fe	μ_3S 2.27(1,3) OC not given	Fe 2.499(8) S 66.6(3,4)	μ_3S,μ_3S 78.3(4,5) μ_3S,Fe 56.7(3,9)	
				$Pt^{II}S_2P_2$	μ_3S 2.32(1,0) Ph_3P 2.29(1,3)	S 94.4(4,8)	μ_3S,μ_3S 75.1(3) PP 99.3(4) μ_3S,P 92.7(3,2.1) 167.4(4,1.6)	
				FeC_3S_2Fe	μ_3S 2.29(1,3) OC not given	Fe 2.506(8) S 66.2(3,6)	μ_3S,μ_3S 75.9(4,3) μ_3S,Fe 56.9(3,7)	
$(\eta^2\text{-phen})Pt(\mu_3\text{-}S)_2\cdot Fe_2(CO)_6$ **(red)**	tr $P\bar{1}$ 2	7.688(1) 11.118(2) 13.257(2)	70.26(1) 76.25(1) 78.68(1)	$Pt^{II}N_2S_2$	η^2N 2.060(6,4) μ_3S 2.262(2,4)	S 93.1(1,3.1)	N,N 80,4(2)[d] μ_3S,μ_3S 74.4(1) N,μ_3S 101.1(2,1) 176.5(2,2)	[177]
				FeC_3S_2Fe	OC not given μ_3S 2.290(3,9)	Fe 2.492(2) S 65.9(1,0)	μ_3S,μ_3S 76.2(1,2) μ_3S,Fe 56.8(1,2)	
$(\eta^4\text{-cod})Pt\mu_3\text{-}S)_2\cdot Fe_2(CO)_6$ **(red)**	tr $P\bar{1}$ 2	7.685(1) 11.363(2) 11.403(2)	113.92(1) 100.57(1) 90.78(1)	PtC_4S_2	η^4C 2.207(11,16) μ_3S 22.287(2,1)	S 91.6(1,1.8)	C,C 35.7(4,4)[e] μ_3S,μ_3S 77.9(1) C,μ_3S 97.7(3,1.6) 162.6(2,5.9)	[177]
				FeC_3S_2Fe	OC not given μ_3S 2.278(3,6)	Fe 2.601(2) S 66.6(1,1)	μ_3S,μ_3S 78.3(1,2) μ_3S,Fe 56.9(1,3)	
$(\eta^4\text{-cod})Pt(\mu_3\text{-}S)_2\cdot Fe_2(CO)_6\cdot$ **(red)**	tr $P\bar{1}$ 2	7.575(1) 11.260(2) 11.274(2)	113.286(4) 100.208(4) 91.500(4)	PtC_4S_2	η^2C 2.193(5,9) 2.226(6,9) μ_3S 2.290(1,2)	Fe 3.285(-,60) S 91.70(5,2.27)	μ_3S,μ_3S 78.10(5)	[178]
				FeC_3S_2Fe	OC not given μ_3S 2.290(1,5)	Fe2.5064(12) S 66.34(5,2)	μ_3S,μ_3S 78.06(5,9) μ_3S,Pt 56.83(4,21)	
$(\eta^5\text{-dcp})Pt(\mu_3\text{-}S)_2\cdot\cdot Fe_2(CO)_6$ **(red)**	m $P2_1/c$ 4	10.501(2) 12.330(3) 15.153(3)	 95.19(3) 	PtC_4S_2	η^4C 2.188(8,9) 2.220(8,10) μ_3S 2.301(2,2)	Fe 3.028(1) S 82.21(8,12) 98.25(8,5)	μ_3S,μ_3S 77.86(7)	[179a]
				FeC_3S_2Fe	OC not given μ_3S 2.291(2,18)	Fe 2.515(2) S 66.58(7,5)	μ_3S,μ_3S 78.89(8) μ_3S,Fe 56.15(7,5)	
[$(\eta^2\text{-dppe})Pt\{(\eta^2\text{-dppe})_2Pt_{0.68}\cdot Pd_{1.32}\cdot(\mu_3\text{-}S)_2\}(Cl)_2\cdot MeCN$ **(yellow)** **(at 160 K)**	tr $P\bar{1}$ 2	14.0572(9) 15.1519(9) 29.5450(19)	90.343(2) 99.877(2) 115.552(2)	MS_2P_2	μ_3S 2.384(1,24) η^3P 2.260(1,14)	M 3.078(1,10) 3.2159(5)	S,S 80.7(1,4) 85.5(1,3)	[179b]
$(Ph_3P)_2Pt(\mu_3\text{-}Se)_2\cdot\cdot Fe_2(CO)_6$ **(red brown)**	m $P2_1/n$ 4	10.944(2) 16.321(3) 23.135(4)	 94.68(1) 	PtP_2Se_2	P 2.293(2,7) μ_3Se 2.452(1,9)	Se 93.1(-,2.6)	PP 100.74(6) μ_3Se,μ_3Se 76.36(2) P,μ_3Se91.55(4,1.64) 166.43(4,37)	[180]
				FeP_3Se_2Fe	OC 1.773(8,10) μ_3Se 2.401(1,7)	Fe 2.533(2) Se 63.65(4,2)	μ_3Se,μ_3Se78.28(4,14) μ_3Se,Fe 58.17(3,25)	
$(\eta^4\text{-cod})Pt(\mu_3\text{-}Se)_2\cdot Fe_2(CO)_6\cdot$ **(red brown)**	tr $P\bar{1}$ 2	7.614(5) 11.320(7) 11.364(7)	91.23(1) 99.52(1) 88.32(9)	PtC_4Se_2	η^4C 2.200(7,11) 2.221(6,9) μ_3Se 2.3983(13) 2.4028(12)	Fe 3.450(-,71) Se 92.05(6,2.5)	not given	[178]
				FeC_3Se_2Fe	OC not given μ_3Se 2.294(1,1)	Fe 2.5377(18) Se 64.00(4,2)	μ_3Se,μ_3Se 78.55(4) μ_3Se,Fe 58.00(4,3)	
$(Ph_3P)_2Pt(\mu_3\text{-}S)_2\cdot V_2(\mu\text{-}S)(\mu\text{-}\eta^2\text{-ptd})\cdot(\eta^5\text{-}C_5H_4Me)_2$ **(dark blue)**	m $P2_1/c$ 4	22.181(7) 13.176(4) 19.303(5)	 111.10 	PtS_2P_2	μ_3S 2.321(2,6) P 2.318(2,20)	S 97.0(1,5)	μ_3S,μ_3S73.65(9) PP 101.31(9) μ_3S,P 92.66(9,1.3)	[181]
				VC_5S_3NV	η^5cpC 1.98(1) μ_3S 2.431(2,1.2) μS 2.263(3) $\mu\eta^2$N 1.990(8)	V 2.556(2) μ_3S 63.66(9,12) μS 68.3(5,3)	not given	
$(\eta^4\text{-cod})Pt(\mu_3\text{-}Te)_2\cdot Fe_2(CO)_6$ **(red)**	tr $P\bar{1}$ 2	7.818(2) 10.507(2) 12.255(3)	103.05(3) 97.57(3) 100.94(3)	PtC_cTe_2	η^4C 2.220(8,0) 2.233(9,11) μ_3Te 2.577(1,5)	Fe 3.62(-,30) Te 79.79(4,5) 99.56(5,3)	μ_3Te,μ_3Te79.08(3)	[178]
				$FeC_3Te_2Fe.$	OC not given μ_3Te 2.576(1,17)	Fe 2.6120(19) Te 60.91(5,6)	μ_3Te,μ_3Te79.34(3,26) μ_3Te,Fe 59.54(5,60)	

Continued **Table 6.** Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with $Pt(\mu_3\text{-}E)_2M_2$ core[a].

COMPOUND (colour)	Crys.cl. Sp.Grp. Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(\eta^2\text{-dppe})Pt(\mu_3\text{-}PPh_2)_2.Fe_2(CO)_6$ (red)	or Pbca 8	17.539(3) 21.490(2) 22.959(3)		PtP_4 FeC_3P_2Fe	η^2P 2.267(3,6) μ_3P 2.318(3,3) OC not given μ_3P 2.255(3,12)	Fe 3.50 P 101.3(1,2.2) Fe 2.617(2) P 56.1(1,4)	P,P 85.5(1)[d] μ_3P,μ_3P 65.7(1) P,μ_3P 104.4(1,1.3) 169.7(1,9) μ_3P,μ_3P 67.7(1,3) μ_3P,Fe 54.5(1,5)	[182]
$[(Ph_3P)Pt(\mu_3\text{-}S)_2.Mn_2(\mu\text{-}CO)(CO)_6].0.5C_6H_{14}$ (red)	tr P$\bar{1}$ 2	12.3163(17) 13.968(2) 15.052(2)	66.559(2) 75.551(3) 72.623(3)	PtS_2P_2 MnC_4S_2Mn	μ_3S 2.350(2,5) P not given OC not given μOC 2.074(13,38) μ_3S 2.327(3,13)	Mn 3.360(1,31) S not given Mn 2.638(2) S not given	not given not given	[183]
$(Ph_2P)_2Pt(\mu_3\text{-}S)_2.Fe_2(NO)_4$ (deep red)	m P2/c 8	20.867(7) 19.616(6) 20.524(4)	113.18(2)	PtS_2P_2 FeN_2S_2Fe	μ_3S 2.459(4,4) P 2.289(4,10) ON 1.66(2,5) μ_3S 2.274(6,23)	Fe 2.887(3) 2.973(3) S not given Fe 2.802(5) S 76.0(3,2)	μ_3S,μ_3S 83.7(3) P,P 99.2(3) μ_3S 85.9(3) N,N 113.4(9,6) μ_3S,μ_3S 90.8(3,6)	[184]
$(Ph_3P)_2Pt(\mu_3\text{-}S)_2.Mn_2(CO)_6$ (green)	m $P2_1/n$ 4	11.0995(7) 16.7179(10) 21.9289(12)	91.149(1)	$PtCS_2P_2$ MnC_3S_2Mn	μ_3S 2.339(1,5) P not given OC not given μ_3S 2.282(2,9)	Mn 2.9109(10) 3.1608(10) Mn 2.8154(14) S not given	not given not given	[183]
$[(\eta^2\text{-dppe})Pt(\mu_3\text{-}S)_2.Ir_2(\eta^5\text{-cp})_2].(BPh_4)_2Me_2CO$	m $P2_1/n$ 4	14.754(3) 22.444(3) 26.854(3)	103.58(1)	PtS_2P_2 IrC_5S_2Ir	μ_3S 2.354(4,8) η^2P2.254(5,2) μ^5cpC not given μ_3S 2.303(5,6)	Ir 2.957(1) 3.038(1) S not given Ir 2.888(1) S not given	μ_3S,μ_3S 83.5(2) P,P 85.5(2)[d] 95.7(2,1) 174.7(2,9) not given	[185]
$(\eta^2\text{-dppe})Pt(\mu_3\text{-}S)_2.Ru_2(N)_2(Me)_4$ (dark orange)	m $P2_1/n$ 4	not given		PtS_2P_2 RuC_2S_2N	μ_3S 2.368(2,3) η^2P 2.264(2) MeC not given μ_3S 2.422(2,3) N 1.607(8,4)	Ru 3.1595(7) S not given Ru 3.2 S not given	μ_3S,μ_3S 80.54(7) μ_3S,P 96.58(7) N,μ_3S 112.5 N,C 104.7	[186]
$(\eta^2\text{-dppe})Pt(\mu_3\text{-}S)_2.Os_2(N)_2(CH_2SiMe_3)_4$ (orange brown)	m $P2_1/c$ 4	not given		PtS_2P_2 OsC_2S_2N	μ_3S 2.3574(14) η^2P 2.2393(16) C not given μ_3S 2.407(1,5) N 1.637(5,10)	Os 3.178 S not given Os .2 S not given	μ_3S,μ_3S 80.55(5) μ_3S,P 97.70(5) N,μ_3S 111.4 N,C 104.9	[186]

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. There are four crystallographically independent molecules.
d. Five-membered metallocyclic ring.
e. Three-membered metallocyclic ring.
f. There are two crystallographically independent molecules

each W-Pt array (W-Pt-W). The mean Pt-W bond distances are 2.713 Å [191] and 2.716 Å [192].

When a pair of μ-PPh_2 ligands serve as a bridge between an M-Pt-M array in such a manner that both PPh_2 ligands are located on the same side (M-Pt-M), the M-Pt-M angles (M=Mn, 159.56(4)º, Mo, 152.5(1)º show the largest deviation from linearity (180º) in this group. The mean Pt-Mn bond distance is 2.744 Å with a mean Pt-P-Mn angle of 74.0º [193,194a]. The Pt-Mo bond distance is 2.866 Å with a mean Pt-P-Mo angle of 53.0º [194b].

There are two PtM_2 derivatives - ruby red M=Fe [195] and red M=Mn [197] - in which a pair of a hydride atoms bridge all Pt-M arrays (M-Pt-M) on the same side with mean Pt-μH bond distances of 1.70(7) Å and 2.00(15) Å, and with mean Pt-H-M bridge angles of 113(5)º and 99(7)º, respectively. The two equidistant Pt-Fe bonds (2.774(3) Å) are about 0.030 Å larger than the Pt-Mn bonds (2.804(3) Å).

A linear Ta(V)-Pt(0)-Ta(V) array (178.8(3)º [196] as well as two Ir(II)-Pt(II)-Ir(II) arrays (180º) [207] are bridged by four Pt(II)-μSR (R=Me [196], C_6F_5 or C_6F_4H [207]) ligands. The mean Pt-S-M bond angles are 70(1)º (M=Ta), 97.2(4) and 97.5(3)º (M=Ir). The mean Pt-Ta bond distance is 2.798(7) Å. For the remaining two $PtIr_2$ derivatives, the data are not given in original paper.

In the dark orange derivative [201] $Pt(NH_3)_2$, two $Pd(\eta^2\text{-en})$ units are connected by a pair of μ-η^3-methylcytosinate-O^2,N^3,N^4 ligands. The nucleobases act as trifunctional ligands towards the metals through the endocyclic N^3 to Pt, the oxygen O^2 and the deprotonated amino group N^4 to Pd. Their mean planes form a dihedral angle of 96.5(1)º. The resulting arrangement for the nucleobases is head-to-tail. The Pd-Pt-Pd angle is 166.79(2)º and the mean Pt-Pd distance is 2.9365(6) Å.

There are two PtM_2 derivatives, yellow $PtCu_2$ [202] and blue $PtCo_2$ [204], in which the M-Pt-M array is

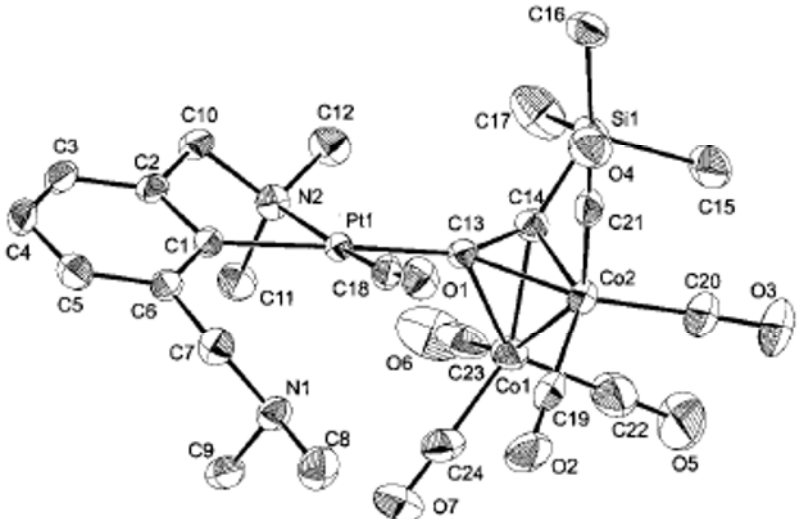

Figure 10. Structure of $(\eta^2\text{-dmap})(OC)Pt(\mu_3\text{-}C{\equiv}CSiMe_3)Co_2(CO)_6$ [211].

bridged by four μC≡CR (R=Ph [202] and Bu^t [204]) ligands. The two equal Pt-M distances are 2.945(2) Å (M=Cu) and 3.077(3) Å (M=Co).

In the red $PtAg_2$ derivative [203], two μ-η^2-maleonitriledithiolate ligands bridge all three metals as $(Ph_3P)_2Ag(I)\text{-}(S)_2\text{-}Pt(II)\text{-}(S)_2\text{-}Ag(I)(PPh_3)_2$. The two equal Pt-Ag distances are 2.996(1) Å. The Pt(II) atom has a square-planar geometry (PtS_4) and Ag(I) atoms are in a distorted tetrahedral environment (AgS_2P_2).

There are three red $PtCo_2$ derivatives [205,206] in which the linear Co(III)-Pt(II)-Co(III) arrays are bridged by four 2-aminoethanethiolate ligands with mean Pt-S-Co bridge angles of 94.6º. Each Pt(II) atom is square-planar (PtS_4) and each Co(III) is tetragonal-bipyramidal (CoN_4S_2).

In the heterotrinuclear $PtCu_2$ derivative [208], two terminal $(MeCN)_2Cu(I)$ fragments are connected to the Pt(II) center by pairs of C≡CPh and η^2-dppy-N,P ligands. The Pt(II) atom has a square-planar (PtC_2P_2) geometry and Cu(I) is five-coordinated (CuN_3C_2). The Pt-Cu distance is 3.250(1) Å.

As already mentioned, there are five PtM_2 derivatives with a linear Pt-M-M (M=Ag [24] and Mo [209]) array (Table 7B). The structure of the pale yellow $PtAg_2$ derivative [24] contains an $[Me_2Pt(\mu\text{-}\eta^3\text{-dppy})_2Ag_2(NCMe)_2]^{2+}$ cation, BF_4^- anions and an MeCN molecule. In the complex cation, two (MeCN)Ag(I) units are connected with the central $PtMe_2$ fragment by two η^3-dppy-N,P,P' ligands. The dppy ligands are trifunctional towards the metals through the P to Pt and the N and P' to Ag association. The resulting arrangement for the dppy ligand is head-tail to head-tail. The Pt-Ag-Ag angle is 169.63(3)º with Pt-Ag and Ag-Ag distances of 2.8190(7) and 2.906(9) Å, respectively.

In four dark green $X_2Pt(\mu\text{-}\eta^3\text{-pyphos})_2Mo_2(\mu\text{-}\eta^3\text{-}RCO_2)_2$ (X=Cl,Br or I; R=Me or Me_3C) complexes [209], a platinum(II) atom sits at an axial position of the Mo-Mo bond and thus the three metal atoms are aligned linearly. The angles of Pt-Mo(1)-Mo(2) in the complexes range from 172.4 to 174.6º. Two cis-arranged pyphos ligands coordinate the platinum atom by their phosphorus atoms and bridge the Mo_2 moiety by two N-O chelations. Two carboxylates also bridge the Mo_2 core in a cis-fashion. The platinum(II) atom in the complexes is in a square-planar arrangement composed of two cis halogen atoms and two cis phosphorus atoms of the pyphos ligands. The Mo-Mo distances range from 2.094(1) to 2.1023(9) Å (av. 2.097 Å), which is about 0.887 Å shorter than the average Pt-Mo(1) distance of 2.984 Å (range 2.956(1) to 3.0035(9) Å).

3.2.5. Unique structures

There are over fifty PtM_2 (M=transition metals) which have complex, unique structures. Their structural parameters are summarized in Table 8. The structure of the $PtRu_2$ derivative [210] contains two tricyclic 1,8-bis(phenylethynyl)napthalene ligands and two metallocycles formed by the coordination of the β-carbon atoms of both ligands to the platinum atom. One ligand is π-bonded to each of the ruthenium atoms. The Ru(1)-Pt-Ru(2) angle is 148.74(7)º and the Pt-Ru bond distances are equal, 2.794(2) Å.

In the yellow $PtMn_2$ derivative [194], the central PtH unit is asymmetrically connected with two terminal $Mn(CO)_4$ units by three μ-PPh_2 ligands as Mn(1)-P-Pt-$(P)_2$-Mn(2), which forms {Mn(1)PPt} three- and {PtP_2Mn(2)} four- membered metallocycles. The Pt-Mn(1) bond distance is 2.847(2) Å and the Pt-P-Mn(1)

Table 7. Crystallographic and structural data for heterotrinuclear PtM_2 (M are transition metals) with a linear PtM_2 array[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: M – Pt - M								
[Pt(μ-η³-mec)$_4$. Cu$_2$(H$_2$O)$_2$]. (NO$_3$)$_2$.3H$_2$O (dark brown)	m C2/c 4	13.938(3) 20.266(4) 12.929(3)	100.22(3)	$Pt^{II}NCu_2$ $Cu^{II}O_3N_2Pt$	μη³N[b] 2.035(11,4) μη³O 2.302(11) 2.386(11) N 1.89(2,1) H$_2$O2.070(2)	Cu 2.519(2,0)	N,N[b]90.0(6,1.0) 175.9(5) Cu,Cu179.31(10) O,O160.6(4) N,N 169.9(7) O,N 95.0(7,6) O,Pt 174.1(3)	[187]
[Pt(μ-η³-mec)$_4$. Cu$_2$Cl$_{1.6}$(H$_2$O)$_{0.4}$]. (NO$_3$)$_{0.4}$.1.6H$_2$O (dark brown)	tr P$\bar{1}$ 2	11.697(4) 13.000(5) 13.315(5)	90.73(3) 116.04(2) 116.20(2)	$Pt^{II}N_4Cu_2$ $Cu^{II}O_2N_2ClPt$	μη³N 2.336(6,5) μη³O 2.336(6,5) 2.399(6,14) N 1.911(7,16) Cl 2.280(4,24)	Cu 2.529(2,2)	N,N 90.0(2,9) 174.6(2,2) Cu,Cu 178.58(3) O,O 158,8(2,2) N,N168.2(3,1) N,Cl 95.9(2,1.7) Cl,Pt 176.3(1,1.4)	[187]
(py)$_2$PtCo$_2$.(CO)$_8$	tr P$\bar{1}$ 1	8.986(12) 9.18(12) 7.426(10)	105.40(20) 107.02(20) 94.54(20)	PtN_2Co_2 CoC_4Pt	pyN 2.02(4) OC 1.77(2,2)	Co 2.613(6)	N,N 180 Co,Co 180 C,C 105(-,1)	[188]
(PhCN)$_2$Pt. {Fe(CO)$_3$(NO)}$_2$ (deep red-brown)	m P2$_1$/c 2	10.458(2) 13.732(5) 8.305(2)	94.00(2)	$Pt^{II}N_2Fe_2$ FeC_3NPt	N 1.946(12,0) OC 1.803(14,17) ON 1.654(13)	Fe 2.657(2,0)	N,N 180 Fe,Fe 180 C,Pt 70.2(5,2.5) 146.6(5) N,Pt 103.7(4)	[189]
[Pt{μ-η²-SP(Ph$_2$). CH$_2$}$_4$Au$_2$Cl$_2$]. Et$_2$O (red)	m P2$_1$/c 4	18.989(3) 13.024(2) 24.191(4)	96.08(1)	$Pt^{II}S_4Au_2$ $Au^{II}C_2ClPt$	μη²S 2.364(6,8) μη²C 2.11(2,2) Cl 2.447(8,5)	Au 2.665(1,3)	S,S 164.6(2,1) Au,Au 180 not given	[190]
Pt(μ-CC$_6$H$_4$Me-4)$_2$. W$_2$(CO)$_4$(η⁵-cp)$_2$ (red-purple) (at 200 K)	m P2$_1$/c 4	12.187(6) 13.404(7) 16.938(9)	96.42(4)	PtC_2W_2 WC_8Pt	μC 2.01(1,1) OC 1.99(1,3) η⁵cpC not given μ 1.91(1,0)	W 2.713(1,2 C 87.5(5,3)	μC,μC 128.8(5) W,W 165.5(0) μC,Pt 47.9(4,2)	[191]
Pt(μ-CMe)$_2$W$_2$. (CO)$_4${η³-HB(pz)$_3$}$_2$ (red)	m P2$_1$/n 4	8.737(2) 10.843(2) 36.345(5)	101.44(1)	PtC_2W_2 WN_3C_3Pt	μC 2.039(9,6) η³N 2.221(7,13) 2.263(7,2) OC 1.985(9,11) μC 1.885(8,3)	W 2.716(1,4) C 87.5(4,1)	μC,μC 133.8(3) W,W 172.8(1) N,N 79.8(3,2.2)[c] μC,Pt 48.6(2,1)	[192]
(py)$_2$PtMn$_2$.(CO)$_{10}$ (red)	m C2/c 4	18.260(18) 7.552(17) 17.204(17)	102.08(10)	PtN_2Mn_2 MnC_5Pt	pyN 2.06(2,0) OC 1.83(2,6)	Mn 2.743(8,0)	N,N 180 Mn,Mn 180 C,Pt 68,94	[188]
(OC)Pt(μ-PPh$_2$)$_2$. Mn$_2$(CO)$_8$ (orange red)	tr P$\bar{1}$ 2	10.240(5) 10.812(4) 17.483(8)	94.89(3) 101.41(5) 121.14(3)	PtP_2CMn_2 MnC_4PPt	μP 2.312(3,7) OC 1.893(7) OC 1.820(13,33) μP 2.239(2,2)	Mn 2.744(1,3) P 74.0(1,3)	μP,μP 101.08(11) Mn,Mn 159.56(4) C,C 90.0(4,9.3) 175.1(4,14)	[193] [194a]
[(OC)P t(μ-PPh$_2$)$_2$. {Mo(CO)$_2$(cp)}$_2$]. 0.5tol (red)	tr P$\bar{1}$ 2	11.706(5) 17.639(8) 10.034(6)	98.20(3) 79.13(2) 102.23(3)	PtP_2CMo_2 MoC_7PPt	μP 2.284(2,4) OC 1.886(11) OC 1.928(12,15) μP 2.357(3) η⁵cpC not given	Mo 2.866(2,6) P not given	P,P 101.3(1) P,Mo 53.0(1,1) C,Mo 76.3(4,6) Mo,Mo 152.5(1) P,Pt 50.7(1,2)	[194b]
(4-Mepy)$_2$Pt(μ-H)$_2$. Fe$_2$(CO)$_4$(η⁵-C$_4$H$_4$. BPh) (ruby red) (at 247 K)	tr P$\bar{1}$ 1	8.532(2) 10.445(3) 10.430(3)	100.75(2) 100.13(2) 101.15(2)	$PtH_2N_2Fe_2$ FeC_6H_2BPt	μH 1.70(7,0) pyN 2.022(7,0) η⁵C 2.06(2,3) η⁵B 2.14(1) OC 1.77(1,7) μH 1.63(9)	Fe 2.774(3,0) H 113(5)	μH,N 86(3) μH,Fe 33(3) N,Fe 87.9(2) C,C 95.2(4) μH,Pt 34(3)	[195]
[Pt(μ-SMe)$_4$Ta$_2$. (η⁵-cp)$_4$](PF$_6$)$_2$ (red orange)	m P2$_1$/c 4	16.44(1) 12.65(1) 17.94(1)	97.8(1)	$Pt^{0}S_4Ta_2$ $Ta^{V}C_{10}S_2Pt$	μS 2.36(3,3) η⁵cpC 2.39(7,9) μS 2.51(3,3)	Ta 2.798(7,11) S 70(1,1)	S,S 109(1,6) Ta,Ta 178.8(3) S,S 104(1,1) S,Pt 106(4,4)	[196]

Continued **Table 7.** Crystallographic and structural data for heterotrinuclear PtM_2 (M are transition metals) with a linear PtM_2 array[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(\mu$-Mepy$)_2$Pt$(\mu$-H$)_2$. $Mn_2(CO)_2(\eta^5$-$C_5H_4Me)$ (deep red)	m $P2_1/n$ 2	10.908(6) 7.818(6) 16.289(7)	 95.42(4) 	$PtH_2N_2Mn_2$ MnC_7HPt	μH 2.00(15) pyN 2.01(2,0) η^5cpC not given OC 1.76(2,3) μH 1.69(15)	Mn 2.804(3,0) H 99(7)	μH,N 103(4) μH,Mn 36(4) N,Mn 90.4(4) C,C 95.1(10) C,Pt 68.5(7) 97.0(7) μH,Pt 45(5)	[197]
$(OC)_2PtRe_2(CO)_{10}$. (bright red)	tr $P\bar{1}$ 1	7.225(2) 10.116(2) 6.503(2)	94.57(2) 91.86(2) 71.59(2)	PtC_2Re_2 ReC_5Pt	OC 1.89(2,0) OC 1.99(1,6)	Re 2.8309(5,0)	Re,Re 180.0 C,Pt 86.7(4,2.1) 178.4(4)	[198]
Pt{μ-η^2-S(Ph_2). $CH_2\}_4Au_2(SO_2)_2$ (red-green) (at 213 K)	tg $I4_1/a$ 4	21.500(8) 14.758(5)	 	$PtIIS_4Au_2$ $AuIC_2SPt$	$\mu\eta^2$S 2.360(3,0) $\mu\eta^2$C 2.088(13,0) O_2S 2.567(6)	Au 2.868(1,0)	S,Au 94.8(1) Au,Au 180 C,S 89.5(3)	[199]
$[(C_6H_{11}NC)($ $C_6H_{11}NH.$ $COC_2H_5)PtMo_2.$ $(CO)_5(\eta^5$-cp$)_2].$ $0.5C_6H_{12}$ (orange)	m $P2_1/c$ 4	14.306(3) 12.609(5) 23.819(3)	 119.11(2) 	PtC_2Mo_2 MoC_8Pt	LNC 1.98(2) LC 2.02(2) OC 1.95(2,4) η^5cpC 2.36(2,5)	Mo 2.889(2)	C,C 178.8(4) Mo,Mo 176.93(4) C,Mo 90.0(4,1.2) C,Pt 53.4(4)- 159.7(5)	[200]
$[(H_3N)_2(\mu$-η^3-. mec$)_2Pd_2.$ $(\eta^2$-en$)_2](NO_3)_4.H_2O$ (dark orange)	or Pbcn 4	20.903(2) 13.510(1) 12.024(1)	 	$PtIIN_4Pd_2$ $PdIIN_3OPt$	$\mu\eta^3$N 2.038(6,1) η^2N 2.017(8,5) $\mu\eta^2$N 2 2.030(7) O 2.034(6)	Pd 2.9365(6,0)	N,N 90.0(2,1) Pd,Pd 166.79(2) N,N 84.0(3)[c] 93.0,172.1(3) N,O 91.1(2,2.0) 171.8(3)	[201]
$(NBu_4)_2[Pt(\mu$- C CPh$)_4Cu_2Br_2]$ (yellow)	tr $P\bar{1}$ 2	12.148(4) 13.977(5) 20.053(4)	84.71(2) 80.8(2) 74.38(3)	$PtIIC_4$ $CuIC_4Br$	μC 2.015(11) 2.020(8) C 2.332(10,6) μC 2.148(11,8) Br 2.298(2)	Cu 2.945(2)	μC,μC 87.5(4) Br,Pt 147.4(1)	[202]
$[Pt(\mu$-η^2-mnt$)_2.$ $Ag_2(PPh_3)_4].$ $2Cl(CH_2)_2Cl$ (red)	tr $P\bar{1}$ 2	13.207(3) 14.194(7) 11.336(3)	98.28(3) 101.67(2) 100.3(3)	$PtIIS_4$ $AgIS_2P_2$	μS 2.297(3) 2.306(3) μS 2.728(3) 3.093(3) Ph_3P 2.476(3,33)	Ag 2.996(1) S not given	μS,μS 90.0(1,5) μS,μS 67.32(9) P,P 116.9(1)	[203]
pt{μ-η^2-SPh$_2$. $PCH_2\}_4Au_2$ (orange red)	tg I4 2	17.348(17) 9.314(17)	 	$PtIIS_4$ $AuIC_2$	$\mu\eta^2$S 2.346(5) $\mu\eta^2$C 2.11(2)	Au 3.034(1,0)	Au,Au 180 C,C 180	[90]
$(NBu_4)_2[Pt(\mu$- C CBu$^t)_4Co_2.$ $Cl_4].1.5Me_2CO$ (blue) (at 173(2)K)	tr $P\bar{1}$ 2	12.54(2) 16.020(11) 19.877(14)	84.40(4) 73.21(5) 70.38(4)	$PtIIC_4$ $CoIIC_4Cl_2$	μC 1.91(2) 2.03(2) C 2.42(2,1) μC 2.21(2,2) Cl 2.248(5,5)	Co 3.077(3)	μC,μC 90.0(8,2.0) μC,μC 76.4(8) C,C 132.4(7) Cl,Cl 106.1(2)	[204]
$[Pt(\mu$-η^2-aet$)_4.$ $Co_2(\eta^2$-en$)_2].$ $Cl_4.6H_2O$ (red brown)	m C2/c 4	14.983(3) 19.857(4) 12.949(3)	 113.51(2) 	$PtIIS_4$ $CoIIIN_4S_2$	μS 2.314(2,2) η^2N 1.999(6,2) μLN 1.988(6,2) μS 2.248(2,3)	 S 94.31(7,23)	μS,μS 90.0(9,6.53) Co,Co 180 N,N 85.4(4,1)[c] 179.1(4) μS,μS 87.2(1,4)	[205]
$Pt(\mu$-η^2-aet$)_4.$ $Co_2(\eta^2$-en$)_2].$ $Cl_4.3H_2O$ (red brown)	or Pbca 4	14.872(3) 14.533(3) 14.347(2)	 	$PtIIS_4$ $CoIIIN_4S_2$	μS 2.317(5,1) η^2N 1.97(2,2) μLN 1.97(2,1) μS 2.243(5,10)	 S 94.7(2,3)	μS,μS90.0(2,7.4) Co,Co 180 N,N 85.3(7) 175.8(7) μS,μS 86.0(2)	[205]
$[Pt(\mu$-η^2-aet$)_2.$ $(\mu$-η^3-pen$)_2.$ $Co_2(\eta^2$-en$)].$ $Cl_2.6H_2O$ (dark brown)	m P2 2	7.836(2) 20.214(1) 10.622(2)	 91.45(1) 	$PtIIS_4$ $CoIIIN_4S_2$ $CoIIIO_2N_2S_2$	μS 2.320(3,2) 2.349(3,4) η^2N 1.990(9,3) $\mu\eta^2$N 1.970(9,1) μS 2.249(3,16) $\mu\eta^3$O1.955(7,15) N 1.937(9,10) μS 2.222(3,15)	 S 95.5(1,1.7)	μS,μS 90.00(9,9.2) Co,Co 180 N,N 85.3(4)[c] 178.1(4) μS,μS 84.8(1) N,N 175.7(4) μS,μS 88.6(1)	[205]
$[Pt(\mu$-η^2-aet$)_4.$ $Co_2(\eta^2$-1,2-pn$)_2].$ $(PF_6)_4.2H_2O$ (dark red)	tg $P4_12_12$ 4	13.253(2) 23.945(4)	 	$PtIIS_4$ $CoIIIN_4S_2$ CuPt	μS 2.312(3) 2.319(3) η^2N 1.992(9,5) $\mu\eta^2$N 1.975(9,3) μS 2.246(3,7)	 S 94.7(1,3)	μS,μS90.00(9,6.7) 173.8(2,9) Co,Co 180 N,N 84.6(4)[c] 90.8(4,1.6) μS,μS 86.8(1)	[206]

Continued **Table 7.** Crystallographic and structural data for heterotrinuclear PtM_2 (M are transition metals) with a linear PtM_2 array[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$Pt(\mu\text{-}SC_6F_5)_4.$ $Ir_2(Cl)_2(\eta^5\text{-}cp^*)_2$ (purple)	m C2/c 8	43.23(7) 10.79(1) 23.93(5)	115.75(9)	$Pt^{II}S_4$	μS 2.293(15,1) 2.335(16,1) μI 2.719(2,26)	S 97.2(4,1.6)	μS,μS90.0(4,8.3) 176.8(5,1) Ir,Ir 180	[207]
				$Ir^{II}C_5S_2SI$	η^5cp*C 2.180(31,40) μS 2.378(16,21) 2.339(16,7) Cl 2.339(12,22)		μS,μS 80.6(4,2) μS,Cl 91.8(5,4)	
$Pt(\mu\text{-}SC_6F_4H)_4.$ $Ir_2Cl_2(\eta^5\text{-}cp^*)_2$ (orange)	m $P2_1/n$ 2	12.180(11) 13.645(14) 16.493(10)	95.86(6)	$Pt^{II}S_4$	μS 2.290(8,1)	S 97.5(3,5)	μS,μS90.0(3,5.4) Ir,Ir 180	[207]
				$Ir^{II}C_5S_2Cl$	η^5cp*C 2.160(29,21) μS 2.397(8,165) Cl 2.340(10)		μS,μS 80.0(3) μS,Cl 91.6(3)	
$[Pt(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)_2.$ $(\mu\text{-}\eta^2\text{-dppy})_2.$ $Cu_2(NCMe)_4].$ $(PF_6)_2$	tr $P\bar{1}$ 1	10.201(1) 11.449(2) 13.937(2)	103.31(1) 104.43(1) 90.60(1)	$Pt^{II}C_2P_2$	μC 2.002(4) $\mu\eta^2$P 2.3189(9)	Cu 3.250(1)	μC,P 86.6(1)	[208]
				$Cu^{I}N_3C_2$	N 2.076(5,17) $\mu\eta^2$N 2.62(4) μC 2.101(4) C 2.173(3)		N,N 101.3(2,2.1)	
B: Pt – M - M								
$[Me_2Pt(\mu\text{-}\eta^3\text{-dppy})_2.$ $Ag_2(NCMe)_2].$ $(BF_4)_2MeCN$ (pale yellow)	tr $P\bar{1}$ 2	13.0418(8) 16.617(1) 17.033(1)	84.402(1) 86.601(1) 72.740(1)	$Pt^{II}C_2P_2Ag$	MeC 2.104(7,9) $\mu\eta^3$P 2.300(2,1)	Ag 2.8190(7)	C,C 82.3(3) P,P 99.88(6) C,P 88.9(2,1.7) 171.2(2,1.7) C,Ag 97.6(3,1.7) P,Ag 83.96(5,1.2)	[24]
				$Ag^{I}N_3PtAg$	LCN 2.244(8) $\mu\eta^3$N 2.377(6) 2.476(6)	Ag^{I} 2.906(9)	N,N 104.9(3) 127.3(3,6.7) N,Pt 87.1(2,2.7) 102.3(2) Pt,Ag 169.63(3)	
				$Ag^{I}P_2NAg$	$\mu\eta^3$P 2.405(2,3) LCN 2.38(2)		P,P 156.15(8) P,N 101.5(4,4) P,Ag 78.35(6,25) N,Ag 176.0(5)	
$Cl_2Pt(\mu\text{-}\eta^3\text{-pyphos})_2.$ $Mo_2(\mu\text{-}\eta^2\text{-}$ $Me_3CCO_2)_2$ (dark red)	tr $P\bar{1}$ 2	13.541(3) 17.029(3) 12.896(3)	101.20(2) 117.00(1) 85.47(2)	$Pt^{II}Cl_2P_2$	Cl 2.332(4,10) $\mu\eta^3$P 2.248(5,3)	Mo 2.956(1)	Cl,Mo 97.0(1,2.1) P,Mo 84.34(9,7)	[209]
				$Mo^{II}O_2N_2.$ Mo	O 2.096(9,1) N 2.18(1,1)	Mo 2.094(1)	O,Mo 90.9(2,4) N,Mo 90.7(3,5) Pt,Mo 174.64(6)	
				$Mo^{II}O_4Mo$	O 2.075(8,11) 2.107(9,13)		O,Mo 93.1(2,2.0)	
$Br_2Pt(\mu\text{-}\eta^3\text{-pyphos})_2.$ $Mo_2(\mu\text{-}\eta^2\text{-}$ $Me_3CCO_2)_2$ (dark red)	tr $P\bar{1}$ 2	12.211(2) 20.859(3) 10.478(2)	98.88(1) 112.55(2) 84.56(1)	$Pt^{II}P_2Br_2$	$\mu\eta^3$P 2.259(2,0) Br 2.470(1,7)	Mo 2.9746(7)	P,Mo 83.68(5,50) Br,Mo 97.16(3,57)	[209]
				$Mo^{II}O_2N_2.$ Mo	O 2.104(5,3) N 2.190(6,18)	Mo 2.0962(8)	O,Mo 91.4(1,6) N,Mo 90.6(1,8) Pt,Mo 173.66(3)	
				$Mo^{II}O_4Mo$	O 2.064(5,9) 2.097(5,19)		O,Mo 93.1(1,2.0)	
$Br_2(\mu\text{-}\eta^3\text{-pyphos})_2.$ $Mo_2(\eta^2\text{-}MeCO_2)_2$ (dark red)	m C2/c 8	34.733(4) 17.81(1) 22.530(5)	124.444(8)	$Pt^{II}P_2Br$	$\mu\eta^3$P 2.258(3,4) Br 2.473(1,13)	Mo 3.001(1)	P,Mo 84.28(8,11) Br,Mo 97.02(5,2.46) Pt,Mo 172.40(5)	[209]
				$Mo^{II}O_2N_2Mo$	O 2.124(9,1) N 2.21(1,0)	Mo 2.096(1)	O,Mo 90.9(5,9) N,Mo 90.5(3,1.5)	
				$Mo^{II}O_4Mo$	O 2.085(9,11) 2.110(9,3)		O,Mo 93.4(2,1.8)	
$I_2Pt(\mu\text{-}\eta^3\text{-pyphos})_2.$ $Mo_2(\eta^3\text{-}Me_3CCO_2)_2$ (dark red)	m $P2_1/c$ 4	13.359(4) 19.686(3) 20.392(4)	107.92(2)	$Pt^{II}P_2I_2$	$\mu\eta^3$P 2.272(2,8) I 2.653(1,16)	Mo 3.0035(9)	P,Mo 83.87(5,26) I,Mo 98.68(3,2.61) Pt,Mo 174.447(3)	[209]
				$Mo^{II}O_2N_2Mo$	O 2.112(5,4) N 2.202(5,10)	Mo 2.1023(9)	O,Mo 90.8(1,1) N,Mo 90.7(1,4)	
				$Mo^{II}O_4Mo$	O 2.077(5,18) 2.105(5,2)		O,Mo 93.2(1,1.1)	

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.

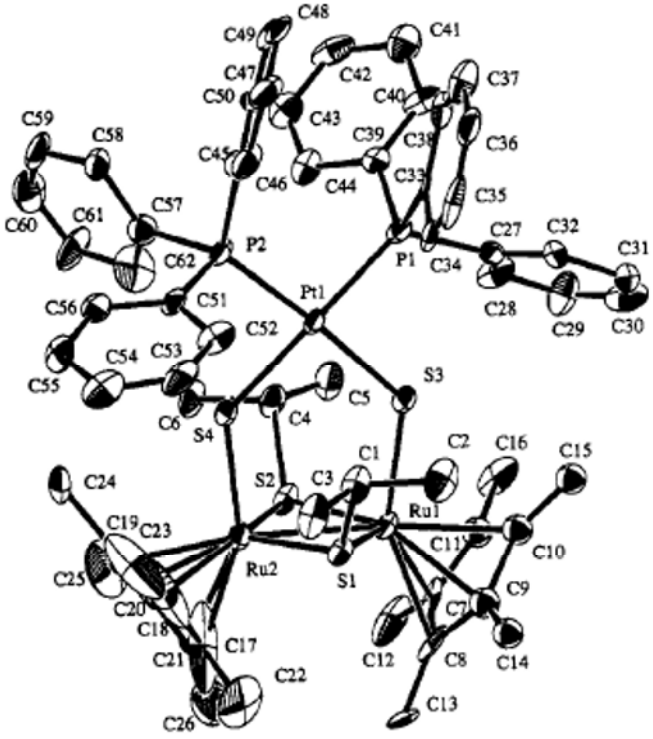

Figure 11. Structure of $(Ph_3P)Pt(\mu\text{-}S)_2Ru_2(\mu\text{-}SPr^i)_2(\eta^5\text{-}cp^*)_2$ [214].

angle is 76.87(15). However, the Pt...Mn(2) distance of 3.618(2) Å rules out a direct metal-metal bond. The mean Pt-P-Mn(2) bridge angles are 101.3º.

The structure of the black $PtCo_2$ derivative [211] is shown in Fig. 10. The coordination environment around the Pt atom reveals a slightly distorted square-planar geometry. The Co-Co bond distance in the tetrahedral (Co_2C_2) framework is 2.4896(9) Å.

In the red $PtFe_2$ derivative [212] the $(OC)_3FeFe(CO)_3$ unit with Fe-Fe bond distance of 2.507(1) Å is connected with the $Pt(PPh_3)_2$ moiety by a sulphide atom, which is coordinated to all three metal atoms. In addition, the HCCPh ligand also serves as a bridge with one carbon atom (CH) between the Pt and Fe(1) atoms and with another carbon atom (CPh) between the Fe(1) and Fe(2) atoms. The platinum(II) atom has a distorted square-planar geometry (PtP_2CS).

The molecular structure of another red $PtFe_2$ derivative [213] can be described as consisting of an Fe_2Se_2 butterfly and a $Pt(Ph_3P)_2$ unit linked by a phenylacetylene fragment which formally can be considered as a four electron donor. The Fe_2Se_2 butterfly adopts a tetrahedral geometry to accommodate the $\{(PhCCH)Pt(PPh_3)_2\}$ unit between the wing-tip Se atoms. The mean μSe-Fe-μSe angle is 80.7º and the Fe-Fe bond distance is 2.534(1) Å. The platinum atom has a distorted square-planar environment (PtC_2P_2).

An asymmetric unit of the dark red $PtRu_2$ derivative [214] consists of two independent molecules, the structures of which are essentially identical. The structure of one is shown in Fig. 11. The cluster has a planar $Pt(\mu\text{-}S)_2Ru_2$ core with Ru-Ru bond distances of 2.767(3) Å in molecule 1 and 2.779(3) Å in molecule 2. The two Ru atoms are additionally constrained by two μ-SPr^i ligands, forming a slightly puckered Ru_2S_2 ring. The dihedral angles between the two Ru_2S planes around the Ru(III)-Ru(III) vector are 173-174º. The coordination geometry around the Pt(II) atom is square-planar (PtS_2P_2).

In the yellow $PtRe_2$ derivative [215], the $(Ph_3P)(OC)PtRe(CO)_4$ moiety with a Pt-Re(2) bond distance of 2.731(1) Å is connected to the $(Ph_3P)(OC)_4Re(1)$ unit by an η^4-C≡C ligand. The ligand is coordinated by one C atom to Pt and Re(2) and by another C atom to Re(1) and Re(2).

The structure of pale the yellow $PtAg_2$ derivative [216] consists of one $Pt(C_6F_5)_2$ fragment $(C{\equiv}CPh)_2$ and two $Ag(PPh_3)$ fragments in a very asymmetric shape. The most remarkable feature is that one of the $Ag(PPh_3)$ units [Ag(1)-PPh_3] is bonded to both alkynyl groups, while the other [Ag(2)-PPh_3] unit is bonded to the platinum atom and to one alkynyl functional group. As a consequence, the two C≡CPh fragments are coordinated differently. The Pt-Ag(2) bond distance of 2.812(2) Å is much shorter than the Pt-Ag(1) bond distance of 3.014(2) Å.

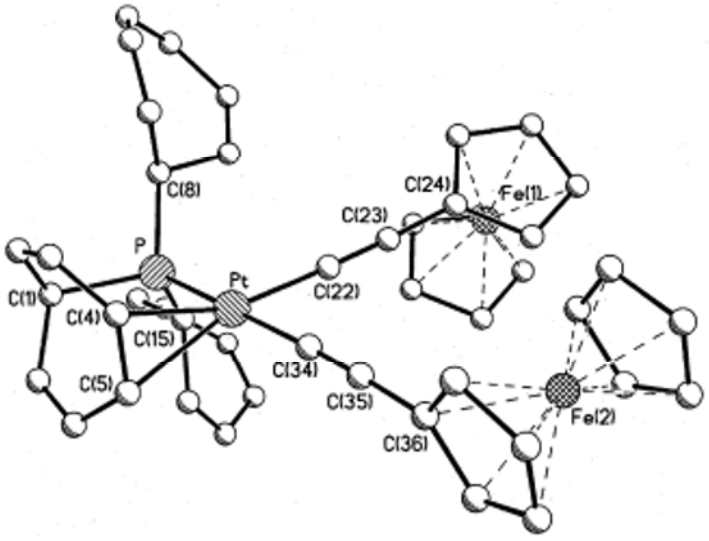

Figure 12. Structure of $[(\eta^3\text{-chy}_3\text{P})\text{Pt}\{(\mu\text{-}\eta^1\text{:}\eta^5\text{-C}\equiv\text{CC}_5\text{H}_4)\text{Fe}(\eta^5\text{-cp})\}_2]$ [238].

In the orange $PtRh_2$ derivative [217] the cis-$[(C_6F_5)_2Pt(C\equiv CBu^t)_2]^{2-}$ fragment acts as a bridging diyne ligand (η^2: η^2) to two nearly identical "Rh(η^4-cod)" units. The two Rh(η^4-cod) units are also bridged by a chlorine atom with the Rh-Cl-Rh bridge angle value of 98.60(14)º. The mean Pt-Rh distance of 3.222(1) Å is about 0.448 Å shorter than the Rh-Rh distance (3.670(1) Å).

There are three bright yellow and red brown $PtOs_2$ [218,219] and three red $PtRe_2$ [220] derivatives in which two terminal M≡N (M=Os or Re) units are connected to the central PtL_2 (L=Me_3P [218] or Cl [219,218]) fragment by nitrido fragments (M≡N-Pt-N≡M). The mean Pr-N-Os bridge angle of 172º (M=Os) is about 5.8º away from linearity (180º) as compared to the Pt-N-Re angles (177.8º). Each Pt(II) atom has a square-planar arrangement (PtN_2P_2 [218] and PtN_2Cl_2 [219,22 220 0]).

In two yellow $PtAg_2$ derivatives [221,222] the central $(C_6Cl_5)_2Pt$ unit is connected with two terminal AgL (L=PPh_3 [221] and PPh_2Me [222]) units by chloride atoms (Ag-Cl-Pt-Cl-Ag), with mean Pt-Cl-Ag bridge angles of 73.6(3)º [221] and 82.63(5)º [222]. The mean Pt-Ag distances are 3.057(2) and 3.131(1) Å, respectively.

In another three cases, one $PtIr_2$ [223] and two yellow $PtMo_2$ [224,225] derivatives, two μ-PX_2 (X=F [223] and HPh [224,225]) units serve as bridges between the two terminal $Ir(CO)(Cl_2(PEt_3)_2$ [223] and $Mo(CO)_5$ [224,225] fragments and a central $PtCl_2$ [223], $Pt(Et_3P)_2$ [224] and Pt(η^2-dppe) [225] unit (M-P-Pt-P-M). Each platinum atom has a square-planar geometry ($PtCl_2P_2$ [223], PtP_4 [224,225]). One of the derivatives [224] contains two crystallographically independent molecules, which differ mostly by degree of distortion (Table 8).

There are four red $PtFe_2$ derivatives [226-228] and one red $PtMo_2$ [229] derivative which contain cyano bridging M-CN-Pt-NC-M chains. Another three red $PtFe_2$ derivatives [226] contain such cyano bridges (Fe-NC-Pt-CN-Fe).

The violet PtM_2 (M=Ni or Fe [230]) derivatives have a similar tetradecker structure. Two terminal M(η^5-cp) fragments are connected with the central platinum by two temdb ligands (η^5:η^5). Each metal atom is sandwiched (PtC_6B_4 and MC_8B_2). The equal Pt-Fe distances of 3.408(3) Å are about 0.185 Å shorter than those of the equal Pt-Ni distances (3.593(2) Å).

In the PtW_2 derivative [231], the cis-$Pt(PEt_3)_2$ unit is connected to two $W(CO)_3(\eta^5\text{-cp})$ fragments by two C≡C-C≡C ligands, which link the three metal centres. The cis-C-Pt-C angle is 86.4(4)º. The Pt(II) atom has a distorted square-planar arrangement (PtC_2P_2).

Two thiamacrocycles were found in the crystal structure of the red $PtFe_2$ derivative [232] formed by a pair of η^2:η^{10}-dcptp ligands and three metal atoms. The central Pt(II) atom has a slightly distorted square-planar geometry. The terminal iron atoms are sandwiched (FeC_{10}).The Pt...Fe distances are 3.996(2) and 4.004(2) Å.

In another eight $PtFe_2$ derivatives, pairs of $cp(Ph)CC_5H_4$ [233] or $Ph_2PC_5H_4$ [242-244] serve as bridges between the metal centers. Each ligand is coordinated to the Pt(II) atom through a P atom and by a cyclopentadienyl ring to the Fe(η^5-cp) unit. Each Pt(II) atom has a square-planar geometry and iron atoms are sandwiched. Two 3-ferrocenylpyridine moieties are coordinated to the $PtCl_2$ unit through N atoms and

Table 8. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with an unique structures[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$(OC)_3Ru(\mu\text{-}\eta^2\text{-bpen})$. $Pt(\mu\text{-}\eta^2\text{-bpen})Ru(CO)_3$	tg $P42_1c$ 4	16.496(3) 17.304(4)		PtC_4Ru_2 RuC_7Pt	μC^b 2.00(11210,4) 2.12(2,0) OC 1.91(2,2) C 2.30(2,0) μC 2.27(2,0)	Ru 2.794(2,0)	Ru,Ru[b]148 .74(7)	[210a]
$(OC)_4Mn(\mu\text{-}PPh_2)Pt$. $(H)(\mu\text{-}PPh_2)_2(CO)_4$ (yellow)	tr $P\bar{1}$ 2	10.941(2) 19.740(5) 10.720(2)	96.13(2) 105.08(2) 105.22(2)	PtP_3HMn MnC_4PPt MnC_4P_2	μP 2.286(4,13) 2.325(4) H not given OC 1.845(21,18) μP 2.306(4) OC 1.827(17,20) μP 2.306(4)	Mn 2.847(2) P 76.87(15) Mn 3.618(2) P 101.28(15,2)	$\mu P,\mu P$69.06(14) 108.27(14) μP,Mo52.09(10) C,Pt 90.2(4,5.3) 113.26(27) 149.55(38) μP,Pt 51.04(6) $\mu P,\mu P$ 76.53(15)	[194a]
$[(\eta^1\text{-}NH_2Me)_2Pt(\mu\text{-}\eta^3\text{-}$ $dmcyt)_2Ag_2]$. $(NO_3)_2$ (colourless)	m $P2_1/n$ 4	7.115(4) 21.365(5) 14.867(8)	94.7(3)	PtN_4Ag AgO_2 AgN_2Pt	η^1N 2.044(9,8) η^3N 2.042(8,3) η^3O 2.259(8,0) η^3N 2.160(9,12)	Ag 2.892(1) 3.040(1)	N,N 90.0(3,1.3) 178.6(3,1) N,Ag 90.0(2,7.2) Ag,Ag 178.85(3) O,O 139.3(3) O,Pt 69.7(2,9) N,N 149.9(3) N,Pt 74.9(2,1.0)	[210b]
$(\eta^2\text{-dmamp})(OC)Pt$. $(\mu_3\text{-}C{\equiv}CSiMe_3)$. $Co_2(CO)_6$ (black)	m $P2_1/c$ 4	10.0863(13) 17.4645(15) 16.437(2)	96.188(10)	PtC_3N CoC_5Co	OC 1.844(4) μ_3C 2.084(4) η^2C 2.062(4) N 2.112(3) OC 1.775(/5) μC 2.008(4) μ_3C 2.069(4)	Co 2.489(9)	C,μ_3C 173(14) C,N 171.68(14) μC, μ_3C37.89(14)	[211]
$[(Ph_3P)_2Pt(\mu_3\text{-}S)$. $(\mu\text{-}HCCPh)$. $Fe_2(CO_6]$.tol (red)	tr $P\bar{1}$ 2	10.973(2) 13.611(4) 19.126(4)	89.51(2) 78.26(2) 67.15(2)	$Pt^{II}P_2CS$ FeC_5SFe FeC_4SFe	Ph_3P 2.274(1) 2.350(1) μC 2.079(4) μ_3S 2.317(1) OC not given μC 2.178(5,39) μ_3S 2.275(1) OC not given μC 1.982(5) μ_3S 2.279(1)	S 104.8(1) Fe 2.507(1) S 66.8(/0)	P,P 97.6(2) $\mu C,\mu_3$S 77.4(1) not given not given	[212]
$(Ph_3P)_2Pt\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}$ $SeC(Ph)C(H)Se\}$. $Fe_2(CO)_6$ (dark red)	tr $P\bar{1}$ 2	11.650(2) 14.368(2) 16.765(2)	67.33(2) 89.33(2) 65.89(2)	PtC_2P_2 FeC_8Se_2Fe	$\mu\eta^2$C 2.103(13,35) Ph_3P not given OC not given μSe 2.365(2,20)	 Fe 2.534(1) Se not given	not given μSe,μSe 80.7(1,4)	[213]
$(Ph_3P)_2Pt(\mu\text{-}S)_2$. $Ru_2(\mu\text{-}SPr^i)_2$. $(\eta^5\text{-}cp^*)_2$[c] (dark red)	tr $P\bar{1}$ 4	22.471(4) 24.353(5) 11.890(1)	93.77(1) 97.48(1) 70.88(1)	$Pt^{II}S_2P_2$ $Ru^{III}C_5S_3Ru$ $Pt^{II}S_2P_2$ $Ru^{III}C_5S_3Ru$	μS 2.324(7,12) Ph_3P not given η^5cp*C not given μS 2.318(7,43) μS 2.332(7,8) μS 2.318(7,2.7)	Ru 4.15(-,2) S not given Ru 2.767(3) S not given Ru 4.15(-,2) Ru 2.779(3)	not given not given not given not given	[214]
$(Ph_3P)(OC)PtRe$. $(\mu\text{-}\eta^2\text{-}C{\equiv}C)Re$. $(CO)_8(PPh_3)$ (yellow)	m $P2_1/c$ 4	15.758(4) 16.123(4) 17.693(5)	95.45(2)	PtC_2PRe ReC_6Pt ReC_5P	OC 1.840(15) μC 2.007(12) Ph_3P 2.320(3) OC 1.964(15,39) μC 2.294(11) 2.565(12) OC 1.953(14,11) 2.052(16) μC 2.139(13) Ph_3P 2.499(4)	Re 2.731(1) C 78.5(4) C 128.6(5)	C,μC 155.3(5) C,P 99.1(4) μC,P 105.5(3) C,Re 100.1(4) μC,Re 55.4(3) P,Re 160.6(1) $\mu C,\mu C$ 28.8(4)[d] μC,Pt 46.1(3) 74.8(13) C,μC 85.0(5) 176.2(5)	[215]

Table 8. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with an unique structures[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
$[(C_6F_5)_2PtAg_2.$ $(\mu_3\text{-}C{\equiv}CPOh).$ $(\mu\text{-}\eta^2, \text{-}C{\equiv}CPh).$ $(PPh_3)_2]0.25CH_2Cl_2$ (pale yellow)	m P2$_1$/c 4	22.650(6) 13.800(3) 19.619(5)	95.55(2)	PtC_4Ag	C not given μC 2.04(2,0)	Ag 2.812(2) 3.014(2) C 82.2(6,1.6)	not given	[216]
				AgCPPt	μC 2.29(2) Ph_3P 2.361(4)		not given	
				AgC_3P	C 2.55(2) μC 2.41(2,4) Ph_3P 2.367(4)		not given	
$(NBu_4)[(C_6F_5)_2Pt.$ $(\mu\text{-}C{\equiv}CBu^t)_2.$ $Rh_2(\mu\text{-}Cl)(\eta^4\text{-}cod)_2]$ (at 200 K)	m C2/c 4	36.629(7) 22.882(5) 28.861(6)	127.21(3)	$Pt^{II}C_4$	C 2.074(13,2) μC 2.00(2,1)	Rh 3.222(1,16) C not given	C,C 91.0(5) μC,μC 98.1(5) C,μC 85.6(5,4)	[217]
				RhC_5Cl	η^4C 2.13(2,3) μC 2.252(13,14) μCl 2.420(4,1)	Rh 3.670(1) Cl 98.60(14)	C,C 95.9(1.9) C,Cl 87.9(2,5)	
$(Me_3P)_2Pt\{(\mu\text{-}N).$ $(OsO_3)\}_2$ (bright yellow)	or Pnma 4	16.162(2) 9.334(2) 11.264(2)		$Pt^{II}N_2P_2$	μN 2.03(4,0) Me_3P 2.27(1,0)	N 169(2)	N,P 86(1,6)	[218a]
				$Os^{VIII}O_3N$	O 1.75(4,4) μN 1.68(4,0)		O,O 116(1,6) O,N 107(1,0)	
$[(p\text{-}Bupy)_2Pt.$ $\{(\mu\text{-}N)(OsO_3)\}_2]$ (yellow)	tr P$\bar{1}$ 1	7.936(1) 10.758(2) 7.738(1)	100.02(1) 99.75(1) 101.75(1)	$Pt^{II}N_4$	pyN 2.040(7,0) μN 1.958(7,0)	N 172.5(5)	N,N 90.0(3,6) 180.0	[218b]
				$Os^{VIII}O_3N$	O 1.713(8,3) 1.745(8) μN 1.681(7)		O,O 110.2(4,1.3) O,N 108.7(4,3)	
$(PPh_4)_2[Cl_2Pt\{(\mu\text{-}N).$ $(OsO_3)\}_2]$ (red brown)	m P2$_1$/n 2	10.5327(7) 13.716(1) 16.159(1)	94.557(7)	$Pt^{II}N_2Cl_2$	μN 1.978(10,0) Cl 2.331(4,0)	N 171.7(6)	N,Cl 91.3(3)	[219]
				$Os^{VI}O_3N$	O 1.720(8,9) μN 1.642(10)		not given	
$(NBu_4)_2[Cl_2Pt\{(\mu\text{-}N).$ $ReCl_4(H_2O)\}_2$ (red)	trg R3 9	36.283(3) 12.314(1)		$Pt^{II}N_2Cl_2$	μN 1.941(6,0) Cl 2.290(2,0)	N 177.3(4)	not given	[220]
				$Re^{VI}Cl_4ON$	Cl 2.351(2,35) H_2O 2.257(6) μN 1.656(6)		not given	
$(NBu_4)_2[Cl_2Pt\{(\mu\text{-}N).$ $ReCl_4(thf)\}_2].thf$ (red)	m C2/c 4	29.813(2) 14.931(1) 16.700(1)	120.27(1)	$Pt^{II}N_2Cl_2$	μN 1.888(7,0) Cl 2.301(3,0)	N 178.4(4)	not given	[220]
				$Re^{VI}Cl_4ON$	Cl 2.341(2,9) thfO 2.260(8) μN 1.695(7)		not given	
$(NBu_4)_2[Cl_2Pt(\mu\text{-}N).$ $ReCl_4(thf)]_2.$ $2CH_2Cl_2$ (red)	tg I4$_1$/a 8	31.867(2) 13.112(1)		$Pt^{II}N_2Cl_2$				[220]
				$Re^{VI}Cl_4ON$				
$(C_6Cl_5)_2Pt\{(\mu\text{-}Cl).$ $Ag(PPh_3)\}_2$ (yellow)	m P2$_1$/a 2	11.538(2) 19.062(4) 12.669(2)	113.66(1)	$Pt^{II}C_2Cl_2$	C 2.059(22,0) μCl 2.317(7,0)	Ag 3.057(2) Cl 73.6(3,6.3)	C,Cl 89.8(6)	[221]
				$Ag^{I}ClP$	μCl 2.447(8) Ph_3P 2.374(8)		Cl,P 148.5(3)	
$(C_6Cl_5)_2Pt\{(\mu\text{-}Cl).$ $Ag(PPh_2Me)\}_2$ (pale yellow)	tr P$\bar{1}$ 1	10.821(3) 12.462(3) 9.268(2)	109.23(2) 99.87(2) 70.85(2)	$Pt^{II}C_2Cl_2$	C 2.052(4,0) μCl 2.323(1,0)	Ag 3.131(1) Cl 82.63(5)	C,Cl 90.0(1,8)	[222]
				$Ag^{I}ClP$	μCl 2.418(2) P 2.370(2)		Cl,P 163.09(5)	
$Cl_2Pt\{(\mu\text{-}PF_2).$ $Ir(CO)Cl_2(PEt_3)_2\}_2$	m P2$_1$/c 4	15.081(12) 10.656(10) 30.485(20)	112.08(5)	$Pt^{II}Cl_2P_2$	Cl 2.348(16,15) μP 2.228(15,15)	P not given	Cl,Cl 90.1(6) P,P 101.9(5)	[223]
				IrP_3Cl_2C	Et_3P 2.431(15) μP 2.292(15,4) Cl 2.403(17,56) OC 1.92(7)		P,P 168.1(5,1.3) P,μP 94.3(6,4.1) Cl,Cl 175.0(23,1.5)	
$(Et_3P)_2Pt\{(\mu\text{-}PHPh).$ $Mo(CO)_5\}_2$ (yellow)	m P2$_1$/a 4	20.027(9) 10.645(4) 20.774(9)	103.00(3)	PtP_4	Et_3P 2.340(6,0) μP 2.407(5,0)	Mo 4.504(5) P 126.1(2)	P,μP 89.5(2,2.2)	[224]
				MoC_5P	OC 1.981(23) 2.052(24,25) μP 2.644(5)		not given	
				PtP_4	Et_3P 2.333(6,0) μP 2.397(4,0)	Mo 4.573(2) P 130.0(2)	P,μP 90.0(2,2.6)	
				MoC_5P	OC 2.648(5) 2.067(25,27) μP 2.648(5)		not given	

Table 8. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with an unique structures[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Á] b [Á] c [Á]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Á]	M - M [Á] M – L - M [°]	L – M - L [°]	Ref
$(\eta^2$-dppe)Pt{μ-PHPh). **$Mo(CO)_5\}_2$** **(yellow)**	m $P2_1/n$ 4	14.295(4) 19.439(6) 18.318(5)	 101.30(2)	PtP_4 MoC_5P	η^2P 2.303(3,4) μP 2.362(3,1) OC not given μP not given	Mo 4.334(2,15) P 122.8(1,7)	PP 84.5(1) μPμP 82.6(1) PμP 96.4(1,2) 177.7(1.3) not given	[225]
[$(\eta^2$-bpy)Pt{$(\mu$-η^2-NC). **$Fe(\eta^2$-dppe)$(\eta^5$-cp)$\}_2$].** **0.5MeOH** **(red)**	tr $P\bar{1}$ 2	14.796(3) 18.158(4) 32.363(6)	88.43(3) 84.34(3) 72.83(3)	$Pt^{II}N_4$ FeC_6P_2	η^2N 1.98(1,2) μCN 1.98(1,1) η^5cpC not given μNC 1.83(2,2) η^2P 2.19(1,2)		not given not given	[226]
$(\eta^2$-bpy)Pt{$(\mu$-η^2-NC). **$Fe(\eta^2$-dppe)$(\eta^5$-cp)$\}_2$** **(red)**	tg $P6_1$ 6	32.120(6) 14.460(3)	 	$Pt^{II}N_2C_2$ FeC_5P_2N	η^2N 2.04(1,1) μNC 1.90(1,1) η^5cpC not given η^2P 2.21(1,2) μCN 1.90(2,2)		not given not given	[226]
[$(py)_2$Pt{$(\mu$-η^2-NC). **$Fe(\eta^2$-dppe)$(\eta^5$-cp)$\}_2$].** **$2Me_2CO$** **(red)**	tr $P\bar{1}$ 1	11.846(2) 11.918(2) 15.130(3)	95.03(3) 91.25(3) 94.73(3)	$Pt^{II}N_4$ $Fe^{VI}C_6P_2$	pyN 2.026(4) μCN 1.956(5) η^5cpC not given μNC 1.839(6) η^2P 2.177(2)		not given not given	[226]
$(py)_2$Pt{$(\mu$-η^2-CN). **$Fe(\eta^2$-dppe)$(\eta^5$-cp)$\}_2$** **(red)**	m C2/c 4	31.215(6) 11.384(2) 25.738(5)	 123.09(3)	$Pt^{II}N_2C_2$ FeC_5P_2N	pyN 2.020(5) μNC 1.980(6) η^5cpC not given η^2P 2.212(4) μCN 1.903(5)		not given not given	[226]
[$(NC)_2$Pt{$(\mu$-η^2-CN). **$Fe(\eta^2$-dppe)$(\eta^5$-cp)$\}_2$].** **CH_2Cl_2** **(red)**	m $P2_1/c$ 2	13.399(3) 14.598(3) 15.895(3)	 101.15(3)	$Pt^{II}C_4$ FeC_5P_2N	NC 1.990(8) μNC 1.993(6) η^5cpC not given η^2P 2.207(4) μCN 1.914(5)		not given not given	[226]
$(Et_3P)_2$Pt{$(\mu$-η^2-NC). **$Fe(\eta^5$-phb)$(CO)_2\}_2$** **(yellow)**	m C2/c 4	20.26(1) 11.355(9) 18.949(9)	 105.45(5)	$Pt^{II}N_2P_2$ FeC_7B	μCN 2.02(1,0) Et_3P 2.259(5,0) OC 1.76(2,1) μNC 1.90(2) η^5C 2.10(2,4) B 2.21(2)		N,N 84.6(8) PP 97.2(3) N,P 89.8(4) C,C 94.3(9,2.5)	[227]
$[(H_3N)_4$Pt{μ-η^2-NC). **$Fe(CN)_5\}_2$].** **$[Pt(NH_3)_4]_2.9H_2O$** **(red orange)**	m $P2_1/c$ 2	15.313(2) 8.353(14) 16.206(5)	 100.52(2)	$Pt^{IV}N_6$ $Fe^{II}C_6$ $Pt^{II}N_4$ (monomer)	H_3N 2.074(13,2) μNC 1.971(11,0) NC 1.924(13,24) μNC 1.883(12) H_3N 2.056(10,11)	Fe 4.993(1)	not given not given not given	[228]
$Cs_2[Pt(\eta^2$-en)$_2Cl_2].$ **$[(\eta^2$-en)$_2$Pt{$(\mu$-NC).** **$Mo(CN)_7\}_2].10H_2O$** **(red)**	tr $P\bar{1}$ 1	9.073(3) 9.856(5) 15.413(5)	80.54(4) 83.99(3) 67.41(4)	$Pt^{IV}N_6$ $Mo^{IV}C_8$ $Pt^{II}N_4Cl_2$ (monomer)	η^2N 2.041(7,2) μCN 1.972(7,0) NC 2.164(9,14) μNC 2.121(8) η^2N 2.048(8,5) Cl 2.301(3,0)		N,N 83.6(3)[e] 90.5(3,1.7) not given N,N 82.7(3)[e] N,Cl 90.0(2,1.1)	[229]
[Pt{$(\mu$-η^5:η^5- **temdb)Ni.** **$(\eta^5$-cp)$\}_2$]** **(violet)**	tg $P4_22_12$ 4	16.847(2) 13.427(2)	 	PtC_6B_4 NiC_8B_2	$\mu\eta^5\mu$C 2.244(15,19) μB 2.303(16,13) η^5cpC 2.140(21,16) $\mu\eta^5\mu$C 2.165(13,16) μB 2.213(24,18)	Ni 3.593(2)	not given	[230]
[Pt{$(\mu$-η^5:η^5- **temdb)Fe.** **$(\eta^5$-cp)$\}_2$]** **(red violet)**	tg $P4_22_12$ 4	16.697(2) 13.204(2)	 	PtC_6B_4 FeC_8B_2	$\mu\eta^5\mu$C 2.204(15,9) μB 2.245(15,13) η^5cpC 2.057(26,26) $\mu\eta^5\mu$C 2.081(14,26) μB 2.139(22,30)	Fe 3.408(2)	not given	[230]
[$(Et_3P)_2$Pt{$(\mu$-η^2-C **≡CC≡C)W.** **$(CO)_3(\eta^5$-cp)$\}_2$].** **$CHCl_3$**[c]	m $P2_1/c$ 8	17.925(2) 21.652(3) 22.686(3)	 101.663(2)	$Pt^{II}C_2P_2$ WC_9	$\mu\eta^2$C 2.00(1,1) Et_3P 2.309(3,6) not given		C,C 86.4(4) PP 100.3(1) C,P 86.8(3,4.3) not given	[231]

Table 8. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with an unique structures[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[Pt{(μ-η²:η¹⁰-dcptp)Fe}₂.(BF₄)₂ (red)	or Pc2₁/n 4	9.995(1) 12.025(2) 27.26(1)		PtS_4 FeC_{10}	μη²S 2.303(12,1) 2.349(12,4) μη¹⁰C not given	Fe 4.000(2,4)	S,S 80.9(4,2) 98.4(4,1.0) 171.8(4,9) not given	[232]
[Cl₂Pt{(μ-η¹:η⁵-nphpcp)Fe.(η⁵-cp)}₂] (orange)	or P2₁2₁2₁ 4	11.8381(3) 19.7931(5) 20.8439(5)		$PtCl_2P_2$ FeC_{10}	Cl 2.369(1,3) μη¹P 2.249(1,7) not given		Cl,Cl 88.87(6) P,P 92.30(5) not given	[233]
[Cl₂Pt{(μ-η¹:η⁵-pycp)Fe(η⁵-cp)}₂].Me₂CO (orange)	tr P$\bar{1}$ 2	9.976(9) 10.53(1) 16.89(1)	106.3(1) 97.8(1) 102.8(1)	PtN_2Cl_2 FeC_{10}	μη¹N 2.025(7,10) Cl 2.295(4,4) not given		N,N 88.5(4) Cl,Cl 91.4(3) N,Cl 90.1(4,5) 177.3(5,4) not given	[234]
[Pt{(μ-η²:η⁵-dmamcp)Fe.(η⁵-cp)}₂] (red)	or Pbca 8	20.400(6) 11.239(3) 25.633(9)		PtN_2C_2 FeC_{10}	μη²N 2.245(6,2) μC 1.971(7,2) not given		N,N 101.9(2) μC,μC 97.0(3) N,μC 80.9(3,7)[e] 173.0(2,1.7) not given	[235]
[(η⁴-cod)Pt{(μ-η¹:η⁵-C₅H₄Cl)Fe(η⁵-C₅H₄Cl)}₂] (orange)	or Pna2₁ 4	22.600(4) 16.048(2) 7.239(2)		PtC_6 FeC_{10}	η⁴C 2.42(20,20) μC 2.022(19,20) η⁵C 2.039(20,41) μC 2.107(20,56)		C,C 83.0(10) not given	[236]
[(Ph₃P)₂Pt{(μ-η¹:η⁵-C≡CC₅H₄)Fe(η⁵-cp)}₂] (red)	m P2₁/n 4	13.100(2) 23.413(3) 16.816(2)	107.338(9)	PtC_2P_2 FeC_{10}	μη¹C 2.000(11,10) Ph₃P 2.312(3,2) not given		C,C 86.3(4) P,P 100.1(1) not given	[237]
[(η³-chy₃P)Pt.{(μ-η¹:η⁵-C≡C.C₅H₄)Fe(η⁵-cp)}₂] (red)	m P2₁/c 4	11.9214(12) 13.7608(13) 24.381(4)	94.574(5)	PtC_4P FeC_{10}	η³C 2.267(8,3) P 2.2721(18) μη¹C 1.987(8,37) not given		C,C 36.0(3)[d] 86.2(3) 104.6(4,3.6) C,P 92.2(2) 177.4(2) not given	[238]
[(η²-dppe)Pt(μ-η²:η¹⁰-docp){Fe(η⁵-cp)}₂][c] (orange) (at 173 K)	tr P$\bar{1}$ 2	11.0890(7) 12.7052(9) 15.1559(10)		PtO_2P_2 FeC_{10}	μη²O 2.038(3) η²P 2.2332(10) not given		O,O 83.92(10)[e] P,P 86.14(4)[e] not given	[239]
[(Me)₃(I)Pt.(μ-η²:η¹⁰-bpvcp).{Fe(η⁵-cp)}₂].2CH₂Cl₂ (deep red) (at 193 K)	m P2₁/n 4	11.497(2) 22.796(6) 15.801(3)	106.08(1)	PtC_3N_2I FeC_{10}	MeC 2.06(2,2) μη²N 2.154(13,21) I 2.8021(13) not given		C,C 87.6(7,2.8) N,N 78.2(5)[e] C,N 94.8(6,3.1) 174.7(6,4) C,I 92.2(5,4) 176.3(5) N,I 87.8(3,2.4) not given	[240]
(dmso)Pt(μ-η¹:η⁵-C≡CC₅H₄)(μ-η²:η⁵-dmat){Fe(η⁵-cp)}₂[c] (orange red)	m P2/c 8	29.924(10) 10.132(3) 19.366(6)	112.810(7)	PtC_2NS FeC_{10}	μη²N 2.141(4) μC 2.023(5) μη¹C 2.059(16) dmsoS 2.1912(14) not given		C,μC 172.4(2) μC,N 82.72(18)[e] C,N 90.03(19) C,S 90.47(16) μC,S 96.68(14) N,S 177.34(13) not given	[241]
[Cl₂Pt{μ-η¹:η⁵-Ph₂PC₅H₄)Fe.(η⁵-cp)}₂].Ch₂Cl₂ (bright yellow)	tr P$\bar{1}$ 1	9.674(1) 11.008(1) 11.735(1)	111.89(1) 104.87(1) 104.97(1)	$PtCl_2P_2$ FeC_{10}	Cl 2.3120(14) μη¹P 2.3179(1) not given		Cl,P 90.00(5,2.04) not given	[242]
[Cl₂Pt{μ-η¹:η⁵-Ph₂PC₅H₄)Fe(η⁵-cp)}₂].2C₆H₆ (dark orange)	tr P$\bar{1}$ 1	9.511(1) 12.754(2) 10.363(1)	97.42(1) 87.45(1) 106.81(1)	$PtCl_2P_2$ FeC_{10}	Cl 2.301(2) μη¹P 2.318(2) not given		Cl 90.00(7,2.44) not given	[243]
[(p-NO₂C₆H₄C≡C)₂Pt.{(μ-η¹:η⁵-Ph₂PC₅H₄).Fe(η⁵-cp)}₂] (yellow)	tr P$\bar{1}$ 1	10.317(1) 10.951(2) 11.768(1)	87.30(1) 68.21(1) 88.38(1)	PtC_2P_2 FeC_{10}	C 2.029(5) μη¹P 2.311(10) not given		Cl,P 90.00(12,5.12) not given	[242]

Table 8. Crystallographic and structural data for heterotrinuclear PtM_2 (M = transition metal) with an unique structures[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
[(p-$NO_2C_6H_4C{\equiv}C)_2$Pt.{(μ-η¹:η⁵-$Ph_2PC_5H_4$).Fe(η⁵-cp)}$_2$] (orange yellow)	or Pbca 4	14.322(1) 16.424(2) 20.627(2)		$Pt^{II}C_2$ FeC_{10}	C 2.033(10) μη¹P 2.313(2) not given		Cl,P 90.0(2,3) not given	[242]
[Cl_2Pt{(μ-η¹:η⁵-$Ph_2PC_5H_4$)Fe..(η^5-$C_5H_4CO_2$)}$_2$]ᶜ (orange)	tr Pī 3	11.041(2) 17.126(3) 18/.961(3)	101.40(1) 105.64(1) 103.11(1)	$Pt^{II}Cl_2P_2$ FeC_{10} $Pt^{II}Cl_2P_2$ FeC_{10}	Cl 2.299(1) μη¹P 2.328(1) not given Cl 2.282(1,13) μη¹P 2.323(1,4) not given		Cl,P 90.00(5,4.29) not given Cl,P 90.00(5,3.68) not given	[244]
[Cl_2Pt{(μ-η¹:η⁵-$Ph_2PC_5H_4$)Fe.(η^5-$C_5H_4CO_2$)}$_2$] 2AcOH (orange)	m $P2_1/c$ 4	10.884(1) 13.307(1) 16.553(1)	96.879(7)	$Pt^{II}Cl_2P_2$ FeC_{10}	Cl 2.308(2) μη¹P 2.340(1) not given		Cl,P 90.00(5,3.89) not given	[244]
[Cl_2Pt{(μ-η¹:η⁵-$Ph_2PC_5H_4$)Fe.(η^5-$C_5H_4CO_2$)}$_2$]. 2CH_2Cl_2 (orange)	m $P2_1/c$ 4	13.9941(9) 16.7920(9) 25.176(1)	118.928(5)	$Pt^{II}Cl_6P_2$ FeC_{10}	Cl 2.340(5,10) μη¹P 2.256(4,1) not given		Cl,Cl 85.8(2) P,P 98.7(2) Cl,P 87.9(2,2.1) 171.9(2,2.3) not given	[244]
[Cl_2Pt{(μ-η¹:η¹⁰-$PhP(C_5H_4)Fe$}$_2$] (dark red)	m $P2_1/n$ 4	18.576(3) 17.409(3) 9.888(2)	96.13(1)	$Pt^{II}Cl_2P_2$ FeC_{10}	Cl 2.354(2,10) μη¹P 2.232(2,5) not given		Cl,Cl 88.11(9) P,P 97.11(7) Cl,P 87.54(8,81) 173.89(8,1.0) not given	[245]
[($Bu^tC{\equiv}C)_2$Pt.{(μ-η²-dppm).AuCl}$_2$] (yellow)	tr Pī 2	9.703(3) 14.362(1) 23.646(3)	75.805(8) 83.87(2) 70.09(2)	$Pt^{II}C_2P_2$ $Au^{I}ClP$	ηC 2.007(7) 2.051(6) μη²P 2.290(2,1) Cl 2.297(3,1) μη²P 2.230(2,2)	Au 3.446(1)	C,C 173.5(3) P,P 175.1(1) C,P 89.5(2,2.5) Cl,P 174.8(1,1.8)	[246]
[Pt{(μ-mnt).Au(PPh_3)}$_2$] (yellow)	m $P2_1/c$ 4	9.149(4) 14.042(7) 17.229(9)	95.26(4)	$Pt^{II}S_4$ $Au^{I}SP$	S 2.290(4) μS 2.289(4) μS 2.326(4) Ph_3P 2.265(4)	S 95.4(1)	S,S 90.00(1,1)ᵉ S,P 180	[247]
[(Ph_3P)Pt{(μ-P_3H).Co(η³-triphos)}$_2$].(CF_3SO_3)$_2$ (dark brown)	tr Pī 2	14.392(13) 14.979(7) 28.472(15)	104.20(4) 97.18(7) 101.11(6)	$Pt^{II}P_4$ CoP_6	Ph_3P 2.299(5) μP 2.311(4,10) μη³P 2.246(5,27) μP 2.289(5,21) P 2.320(5,11)	P 126.8(2)	μP,μP 66.4(2)ᵍ 83.8(2) μP,P104.9(2,1.7) μP,μP 56.9(2,2)ᵈ 66.9(2)	[248]
[(H_3N)$_2$Pt{(μ-η²-mec)Pd(η³-dien)}$_2$].(ClO_4)$_4$.2H_2O (pale yellow)	or Pbca 4	10.451(3) 14.908(6) 27.904(4)		$Pt^{II}N_4$ $Pd^{II}N_4$	H_3N 2.046(10) μη²N 2.047(8) η³N not given μη²N 2.047(8)	Pd 5.13	N,N 90.0(4,5) not given	[249]
[(C_6F_5)$_2$Pt{(μ-η³-SCS_2)Pd(η²-dppc)}$_2$].CH_2Cl_2 (yellow)	trg $P3_221$ 3	14.636(2) 29.237(4)		$Pt^{II}C_2S_2$ $Pd^{II}S_2P_2$	Cl 2.072(6) μη³S 2.338(5) μη³S 2.349(4,8) η²P 2.278(4,3)		C,C 87.60(5) S,S 89.8(2) C,S 91.4(3) 176.2(3) S,S 74.8(2)ᵍ P,P 85.5(2)ᵉ S,P 99.7(2,8) 173.3(2,1.7)	[250]

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. There are two crystallographically independent molecules.
d. Three-membered metallocyclic ring.
e. Five-membered metallocyclic ring.
f. Six-membered metallocyclic ring.
g. Four-membered metallocyclic ring.

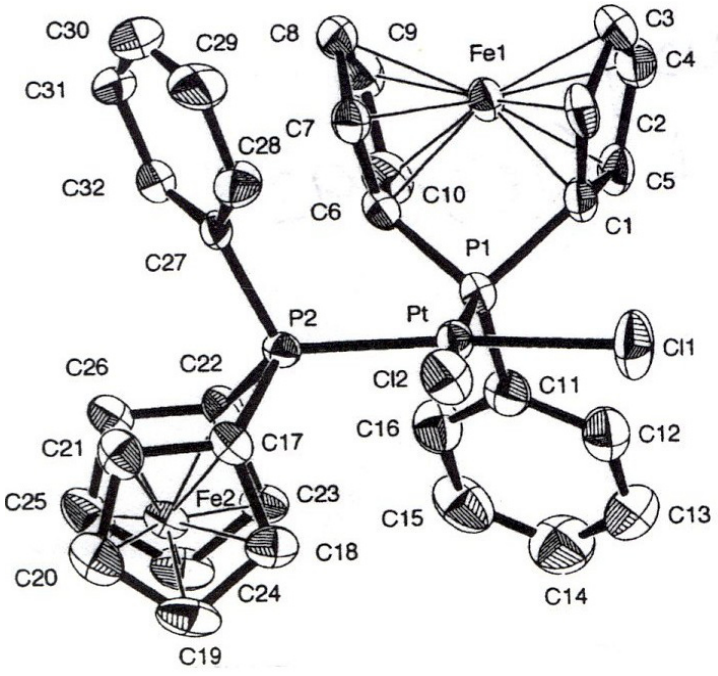

Figure 13. Structure of $[Cl_2Pt\{(\mu\text{-}\eta^1\text{:}\eta^{10}\text{-}PhOP(C_6H_4)_2Fe\}_2]$ [245].

complete a square-planar environment about the Pt(II) center (PtN_2Cl_2).

In the red $PtFe_2$ derivative [235], two terminal Fe(η^5-cp) fragments are connected to the Pt(II) centers by a pair of μ-$\eta^2\eta^5$-dmamcp ligands. The ligands are coordinated to the Pt(II) center through N and one C atom. This C atom along with another four C atoms sandwiches the iron atoms.

Two 1,1'-dichloroferrocene moieties are connected to Pt(η^4-cod) through one C atom of each moiety, which serve as a bridge with a cis-C-Pt-C angle of 83.0(10)º [236]. There are two red $PtFe_2$ derivatives [237,238] in which two terminal Fe(η^5-cp) fragments are connected with the $Pt(PPh_3)_2$ [237] and Pt(η^3-chyP) [238] centers by a pair of μ-η^1:η^5-$C{\equiv}CC_5H_4$ ligands. The structure of latter is shown in Fig. 12. As can be seen, a chelating $P(chy)_2$(η^2-chy) ligand is coordinated through both the phosphorus atom and the central double bond of one cyclohepta-2,4,6-trienyl substituent. In the orange $PtFe_2$ derivative [239], a rigid C_2-symmetric bis(ferrocenyl)diol ligand is coordinated to the Pt(η^2-dppe) unit through two O atoms and completes a slightly distorted square-planar geometry about the Pt(II) atom (PtO_2P_2). A 4,4'-bis(ferrocenylvinyl)-2,2'-bipyridine uses both N atoms for coordination to the $Pt(Me)_3I$ unit and creates an octahedral arrangement about the Pt(IV) atom in the deep red complex [240]. The Pt...Fe separations are 10.133 and 10.225 Å, respectively. In the orange red $PtFe_2$ derivative [241], η^1:η^5-$C{\equiv}CC_5H_4$ and η^2:η^5-dmat ligands connect the central Pt(dmso) unit (the former ligand through a C atom and the latter by C and N atoms) with two Fe(η^5-cp) fragments, through five carbon atoms. The Pt(II) atom has a slightly distorted square-planar environment (PtC_2NS) and iron atoms are sandwiched (FeC_{10}). The structure of the dark red $PtFe_2$ derivative [245] is shown in Fig. 13. As can be seen, two ferrocene units are each located above or below the square-planar coordination plane to avoid steric congestion.

In the yellow $PtAu_2$ derivative [246], a trans-Pt $(C{\equiv}CBu^t)_2$ and two AuCl fragments are bridged by two η^2-dppm ligands. The platinum(II) and gold(I) centres show square-planar and linear coordination geometries. The structure is subject to considerable strain, arising from steric interactions of the bulky ligands and balanced by substantial angular distortions: Pt-P(1)-C(13)-P(2) 179.2(5)º, Pt-P(3)-C(38)-P(4) 67.8(3), Au(1)-P(2)-C(13)-P(1) 21.8(3)º and Au(2)-P(4)-C(38).P(3) -40.0(3)º.

In another yellow $PtAu_2$ derivative [247], two $Au(PPh_3)$ units are connected to the Pt(II) center by two maleonitriledithiolate ligands. The Pt(II) atom has a square planar geometry (PtS_4). The two AuSP linear units are each located above or below the square-planar coordination plane, with a Pt-S-Au angle of 95.4(1)º.

The structure of the dark brown $PtCo_2$ derivative [248] consists of a well separated $[(Ph_3P)Ot\{(\mu\text{-}P_3H)Co(\eta^3\text{-triphos})\}_2]^{2+}$ cation and $CF_3SO_3^-$ anions. The structure of the complex cation is shown in Fig. 14. The assembly of the two $[(\eta^3\text{-triphos})Co(P_3H)]^+$ cations is

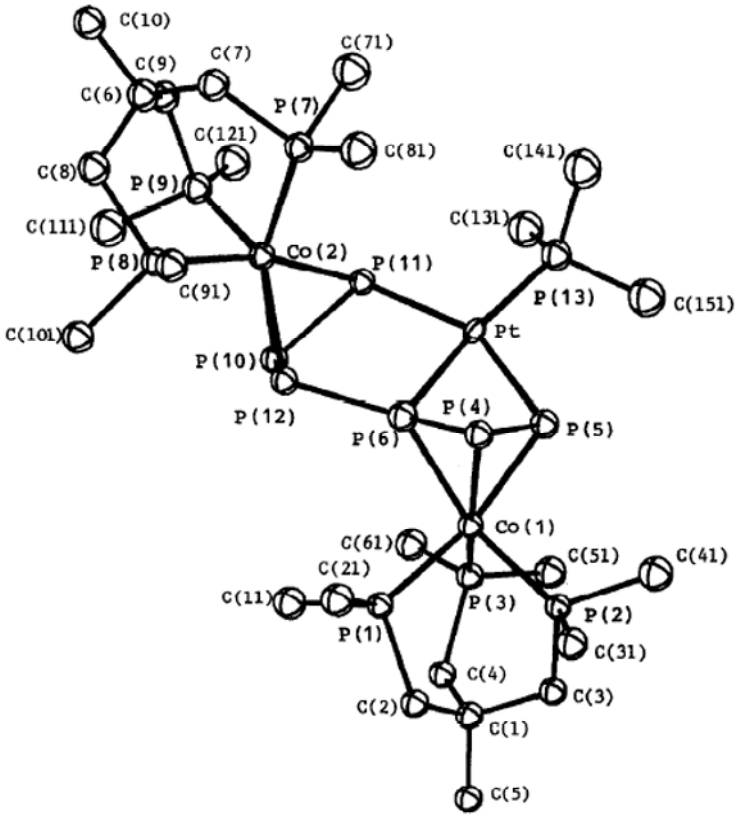

Figure 14. Structure of $[(Ph_3PPt\{(\mu\text{-}P_3H)Co(\eta^3\text{-triphos})\}_2]^{2+}$ [248].

attained through the formation of a P-P bond between phosphorus atoms of their P_3 groups. The platinum has a distorted square-planar coordination and the cobalt has a distorted octahedral coordination.

The X-ray structure of the pale yellow $PtPd_2$ derivative shows [249] a head-to tail and anti-, anti-arrangement of the two 1-methylcytosinates. The Pd atoms coordinate to the two endocyclic N3 atoms and thus stabilize the anti conformation of the two nucleobases. The nucleobases are almost perpendicular to the Pt coordination plane (88.2(4)°). Two trans NH_3 ligands complete a square-planar coordination about the Pt(II) atom (PtN_4), while the terdentate dien ligands carry out the same role about the Pd(II) atom (PdN_4).

In the yellow $PtPd_2$ derivative [250], two terminal $Pd(\eta^2\text{-dppe})$ fragments are connected to the $Pt(C_6F_5)_2$ unit by a pair of SCS_2 ligands. The Pt(II) atom lies on a crystallographic two-fold axis and is in an approximately cis square-planar environment, formed by one carbon of each C_6F_5 group and the terminal sulphurs of both SCS_2 groups (PtC_2S_2). The paladium(II) atoms are also in a distorted square-planar environment formed by chelating the dppe ligand with a "bite" P-Pd-P angle of 85.5(2)° and also by chelating the S_2CS ligand with a "bite" S-Pd-S angle of 74.8(2)°.

Inspection of the data in Table 8 reveals that the derivatives have the following types of crystal classes: monoclinic (x22) > triclinic (x17) > orthorhombic (x7) > tetragonal (x5) > trigonal (x2). There are fourteen different transition metals of which iron is by far the most prevalent, with twenty seven examples. The other are rhenium (x4), silver, molybdenium and osmium (each x3), gold, cobalt, ruthenium and paladium (each x2); tungsten, manganese, nickel, rhodium and iridium (each x1).

Two crystallographically independent molecules in the same crystal were found in six derivatives: $PtRu_2$ [214], $PtMo_2$ [224], PtW_2 [231] and $PtFe_2$ [239,241,244], which differ mostly by degree of distortion and are classical examples of distortion isomers [37].

4. PtMM' compounds

There are twenty four coloured PtMM' clusters (monoclinic (x13), triclinic (x10) and one orthorhombic). Their crystallographic and structural parameters are gathered in Table 9. In seven clusters [251-257] (Table 9A), the three metal atoms form a triangle with the mean M-M bond length increasing in the order:

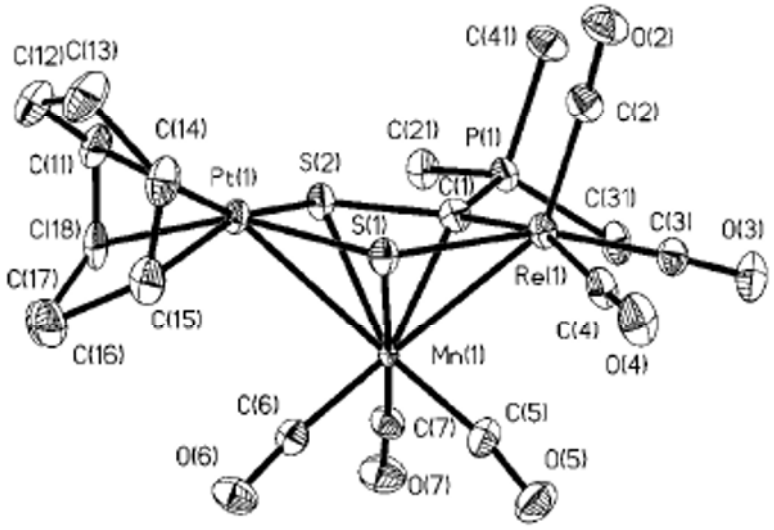

Figure 15. Structure of [(η⁴-cod)Pt(μ_3-S)(μ-SCPcy$_3$)Mn(CO)Re(CO)$_3$ [261].

2.542 Å (PtCoPd) [251] < 2.700 Å (PtFeW) [252,253] < 2.711 Å (PtFeW) [253] < 2.745 Å (PtWCu) [254] < 2.746 Å (PtMoRh) [255] < 2.817 Å (PtAuW) [256] < 2.842 Å (PtAuW) [257]. The shortest Pt-M and M-M bond distances are 2.530(2) Å for Pt-Co [251] and 2.801(2) Å for W-Au [257]. The maximum deviation from the acute M-M-M bond angle of 60º increases in the sequence: 0.7º [251] < 1.9º [256] < 3.4º [254] < 4.1º [257] < 5.6º [252,253] < 6.5º [253] < 8.1º [255], which reflects distortion of the respective triangle.

Molecules of another five clusters [258-261] contain an open trimetallic (Pt-M-M') array (Table 9B). In two of them [258], the molecules are comprised of the Pt(CO)(PPh$_3$) or Pt(PPh$_3$)$_2$, Fe(CO)$_3$ and Ru(CO)(cp) fragments that are Pt-Fe-Ru bonded in an open trimetallic array. The metal-metal bonds (Pt-Fe 2.528(2) Å and Fe-Ru 2.761(2) Å in one and 2.696(2) and 2.639(2) Å in another) are supported by a μ_3-η^1:η^2:η^3-allenyl ligand. The Pt-Fe-Ru bond angle is 84.1(1)º and the Pt...Ru separation is 3.55 Å.

In the dark green PtFeMn cluster [259], which contains two crystallographically independent molecules, the Pt-Fe-Mn bonds (Pt-Fe, 2.617(3) / 2.632(2) Å and Fe-Mn, 2.676(3) / 2.692(3) Å) are supported by a μ_3-C=CHPh ligand. The μ_3-C=CHPh ligand is η^1-bonded to the Mn and Fe atoms and η^2-coordinated to the Pt. The Pt...Mn separations are 3.512(3) and 3.718(3) Å, respectively.

In the dark brown Pt-Ru-Ti derivative, the bonds (Pt-Ru, 2.9043(8) Å and Ru-Ti, 2.836(2) Å) [260] are supported a by μ_3-S atom. In addition, the former bond is also supported by a μ-H atom and the latter by a μ-Cl atom. The Pt...Ti separation is 3.331(2) Å.

The structure of the orange PtMnRe cluster [261] is shown in Fig. 15. A molecule contains an angular Pt-Mn-Re framework with Pt-Mn (2.956(1) Å) and Re-Mn (2.822(1) Å) bonds. The SCPcy$_3$ and S ligands act as bridges between the three metal centers. The Pt-S(2)-C(1) ring is planar; the highest deviation occurs with Re(1), which is 0.115(3) Å out of plane.

There are six coloured examples [262-266] which contain an M$_3$ chain core (Table 9C). The structure of the bright yellow PtSnFe complex [262] contains a bent Pt-Sn-Fe array (115.8(1)º) whose terminal metal atoms are bridged by μ-η^2-dppm. The Pt-Sn bond distance of 2.524(2) Å is shorter than that of Sn-Fe (2.568(2) Å). Another bright yellow complex [262] is characterized by a bent Pt-Hg-Fe chain (164.7(2)º). The value of the Pt-Hg bond distance of 2.575(2) Å is about 0.059 Å shorter than that of Hg-Fe (2.634(6) Å).

There are two yellow complexes [263,264] in which the mercury atom shows an almost linear coordination (PtHgM). In the former [263] the Pt-Hg-W angle is 171.9(1)º and the Hg-Pt and Hg-W bond distances are 2.572(1) and 2.755(1) Å, respectively. The latter [264] contains two crystallographically independent molecules with Pt-Hg-Mn angles of 178.20(11) and 178.96(19)º. The Hg-Pt and Hg-Mn bond distances are 2.590(2) and 2.618(4)º in one and 2.605(2) and 2.647(5) Å in the other molecule.

The X-ray structure of the orange PtWRe complex shows [265] that the molecule has a bent Pt-W-Re (151.3(1)º) spine, with metal-metal distances Pt-W 2.771(1) and W-Re 3.082(1) Å. The W-Pt bond is bridged by the CC$_6$H$_4$Me-4 group.

The molecular structure of the orange IrPtRh complex [266] confirms the presence of formally

Table 9. Crystallographic and structural data for heterotrinuclear PtMM' clusters[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
A: M_3 - TRIANGLE								
Pt(μ-η^2-dppm)$_2$. Co(CO)$_3$PdCl (red)	m $P2_1/n$ 2	12.291(3) 19.321(4) 23.680(5)	 100.05(2)	PtP_2CoPd CoC_3PPtPd $PdClPPtCo$	P[b] 2.256(6,21) OC 1.79(3,15) P 2.197(5) Cl 2.464(7) P 2.232(6)	Co 2.530(2) P d 2.560(2) Pd 2.537(3)	P,P[b] 107.5(2) Co,Pd 59.8(1) Pt,Pd 60.7(1) Pt,Co 59.5(1)	[251]
(PEt$_3$)(CO)Pt. (μ_3-CC$_6$H$_4$Me-D). Fe(CO)$_3$W(CO)$_2$(cp) (dark brown) (at 220 K)	or $Pna2_1$ 4	16.010(7) 8.954(8) 18.450(9)		PtC_2PFeW FeC_4PtW WC_8PtFe	OC 1.90(2) μ_3C 2.23(2) Et_3P 2.254(3) OC 1.78(2,4) μ_3C 1.90(2) OC 2.01(3,1) μ_3C 2.00(2) η^5cpC 2.34(3)	Fe 2.542(3) C 75.5&(7) W 2.775(1) C 81.7(7) W 2.784(3) C 91.1(8)	C,μ_3C 113,4(8) C,P 98.8(7) μ_3C,P137.9(5) Fe,W 63.0(1) Pt,W 62.6(1) Pt,Fe 54.4(1)	[252] [253]
(PMePh$_2$)$_2$Pt. (μ_3-CC$_6$H$_4$Me-4). Fe(CO)$_3$W(CO)$_2$(cp) (red brown) (at 200 K)	m $P2_1$ 2	10.005(2) 17.240(3) 12.928(4)	115.98(2)	PtP_2CFeW FeC_4PtW WC_8PtFe	P 2.310(4,21) μ_3C 2.11(1) OC 1.79(1,2) μ_3C 1.96(1) OC 1.96(2,1) μ_3C 2.02(1) η^5cpC 2.36(2)	Fe 2.556(2) C 77.6(5) W 2.883(1) C 88.4(5) W 2.694(2) C 85.1(4)	P,Fe 102.2(1) 153.2(1) P,W 105.3(1) 134.2(1) Fe,W 59.0(1) Pt,W 66.5(1) Pt,Fe 54.4(1)	[253]
(PMe$_3$)$_2$Pt(μ_3-CC$_6$H$_4$Me-4). W(CO)$_2$(cp)Cu(cp*) (bleck)	m $P2_1/c$ 4	10.516(5) 17.898(8) 18.134(6)	94.25(3)	PtP_2CWCu WC_8PtCu CuC_6PtW	P 2.313(7,28) μ_3C 2.00(2) OC 1.95(3,3) μ_3C 2.03(2) η^5cpC 2.42(4) μ_3C 1.96(2) η^5cp*C 2.27(3)	W 2.779(2) C 87.2(7) Cu 2.807(2) C 90.3(8) Cu 2.648(3) C 83.2(7)	P,P 98.3(2) W,Cu 56.6(1) Pt,Cu 62.2(1) C,W 49.6(5) Pt,W 61.2(1)	[254]
(PPh$_3$)Pt(μ-PPh$_2$). Mo(cp)(μ-CO)$_2$(μ-C$_6$H$_5$)Rh(PPh$_3$) (dark green)	m $P2_1/n$ 4	11.116(2) 16.902(3) 27.792(5)	93.84(1)	PtP_2CRhMo RhC_4PPtMo MoC_7PtRh	P 2.246(2) μP 2.296(2) μC 2.070(8) μOC 2.165(9,24) μC 2.070(8) C 2.412(8) Ph_3P 2.250(2) μO 2.021(8,8) η^5cpC 2.334(7)	Rh 2.662(1) C 77.9(2) Mo 2.958(1) P 78.4(1) Mo 2.619(1)	μC,μP 159.1(2) P,Rh 147.4(1) Rh,Mo 55.3(1) P,Pt 174.2(1) Pt,Mo 68.1(1) Rh,Pt 56.6(1)	[255]
[(Pcy$_2$H)(CO)Pt. (μ-Pcy$_2$)W(CO)$_2$. (cp)Au(PPh$_3$)]PF$_6$ (yellow)	tr $P\bar{1}$ 2	14.358(7) 15.796(6) 12.462(6)	105.57(2) 98.18(2) 98.21(2)	PtP_2CAuW WC_7PtAu AuPPtW	P 2.335(7) μP 2.303(7) OC 1.86(2) OC 1.93(2,5) η^5cpC not given Ph_3P 2.305(6)	W 2.827(2 P 73.2(2) Au 2.860(2) Au 2.763(2)	μP,W 55.5(2) μP,Au 77.0(2) W,Au 58.1(1) Pt,Au 61.5(1) Pt,W 60.3(1)	[256]
(PMe$_3$)$_2$Pt(μ_3-CC$_6$H$_4$Me-4). W(CO)$_2$(cp)Au(PMe$_3$)	tr $P\bar{1}$ 2	10.920(8) 11.237(7) 15.002(17)	90.18(7) 113.63(9) 91.79(6)	PtP_2CWAu WC_8PtAu AuCPW	P 2.29(1,3) μ_3C 1.97(4) OC 1.89(4,1) η^5cpC 2.36(4) μ_3C 2.01(4) μ_3C 2 2.21(4) P 2.27(1)	W 2.770(2) C 88(2) Au 2.956(2) C 90(2) Au 2.801(2) C 83(3)	P,P 97.5(5) W,Au 58.5(1) Pt,Au 64.1(1) W,Pt 57.4(1)	[257]

Continued **Table 9.** Crystallographic and structural data for heterotrinuclear PtMM' clusters[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
B: OPEN Pt – M - M' ARRAY								
$(Ph_3P)(OC)Pt.\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C(Ph)=C=CH_2\}Fe(CO)_3.Ru(CO)(\eta^5\text{-}cp)$ (orange)	m $P2_1/n$ 4	8.433(1) 33.608(8) 12.181(2)	99.62(2)	PtC_2PFe	OC 1.874(12) μC 2.022(9) Ph_3P 2.291(3)	Fe 2.528(2) C not given Ru 3.55	C,μC 158.0(5) C,P 97.3(4) μC,P 104.4(3) C,Fe 104.4(4) μC,Fe 54.0(3) P,Fe 158.4(1)	[256]
				FeC_5PtRu	OC 1.770(12,22) μC 1.98(10) 2.116(10)	Ru 2.761(2) C not given	Pt,Ru 84.1(1)	
				RuC_8Fe	OC 1.832(13) C 2.214(9) μC 2.116(9)		not given	
$(Ph_3P)_2Pt(\mu_3\text{-}\eta^1\text{:}\eta^2.O^2\text{-}C(Ph)=C=CH_2).Fe(CO)_3(\mu\text{-}CO)Ru.(CO)(\eta^5\text{-}cp)$ (orange)	m $P2_1/n$ 4	16.724(4) 13.636(3) 20.264(4)	96.84(2)	PtP_2CFe	Ph_3P 2.258(4) 2.299(4) μC 2.062(15)	Fe 2.696(2) C not given	P,P 101,9(1) P,μC 96.0(4) 161.9(4) P,Fe 115.8(1) 138.6(1) μC,Fe 46.4(4)	[256]
				FeC_6PtRu	OC 1.786(18,38) 2.141(16) μOC 1.918(16) $\eta^2\mu$C 2.001(16,36)	Ru 2.639(3) C not given	Pt,Ru 125.9(1)	
				RuC_8Fe	OC 1.849(17) μOC 2.125(17) μC 2.102(13) η^5cpC not given		not given	
$[\{\eta^1Ph_2PCH_2P(=o)Ph_2\}.(CO)Pt(\mu_3C=CHPh).Fe(CO)_3Mn(CO)_2(cp)].0.5C_5H_{12}$[c] (dark green)	tr $P\bar{1}$ 2	13.646(9) 18.496(8) 19.099(9)	76.55(3) 70.96(3) 73.33(3)	PtC_3PFe	OC not given C 2.24(1) μ_3C 2.24(1)	Fe 2.617(3) Mn 3.512(3)	not given	[257]
				FeC_4PtMn	OC not given μ_3C 1.88(1)	Mn 2.676(3) C 88.5(5)	Pt,Mn 83.14(9)	
				MnC_8Fe	OC not given η^5cpC not given μ_3C 1.95(1)		not given	
				PtC_3PFe	OC not given C 2.18(1) μ_3C 2.23(1)	Fe 2.632(2) Mn 3.718(3)	not given	
				FeC_4PtMn	OC not given μ_3C 1.84(1)	Mn 69.2(3) C 90.2(5)	Pt,Mn 88.57(9)	
				MnC_8Fe	OC not given η^5cpC not given μ_3C 1.96(1)		not given	
$(PPh_3)_2Pt(\mu\text{-}H)(\mu_3\text{-}S).Ru(cp^*)(\mu\text{-}S)TiCl(cp)$ (dark brown)	m $P2_1/n$ 4	11.369(2) 16.207(3) 26.116(2)	102.29(1)	PtP_2HSRu	P 2.303(2,21) μH 1.79 μ_3S 2.341(2)	Ru 2.9043(8) S 77.01(7) Ti 3.331(2) S 90.34(9)	not given	[258]
				RuC_5S_2HTi	η^5cp*C not given μ_3S 2.324(2) μS 2.361(3) μH 1.69	Ti 2.836(2) μ_3S 74.62(8) μS 76.65(9)	Ti,Pt 70.93(4)	
				TiC_5S_2ClRu	η^5cpC not given μ_3S 2.355(3) μS 2.208(3) Cl 2.336(3)		not given	
$[(\eta^4\text{-}cod)Pt(\mu_3\text{-}S).(\mu\text{-}SCPcy_3)Mn(CO)_3.Re(CO)_3]0.5CH_2Cl_2$ (orange)	m $P2_1/n$ 4	8.845(2) 15.133(3) 24.102(5)	not given	PtC_4S_2Mn	η^4codC not given μ_3S 2.290(2) μS 2.272(2)	Mn. 2.9563(13)	S,S 88.89(9)	[259]
				MnC_4S_2PtRe	OC not given μC 2.220(10) μ_3S 2.479(3) μS 2.426(3)	Re 2.8216(13)	Re,Pt 90.42(4)	
				ReC_4SMn	OC not given μC 2.115(9) μ_3S 2.428(2)		μC,S 84.9(3)	

Continued **Table 9.** Crystallographic and structural data for heterotrinuclear PtMM' clusters[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
C: M_3 CHAIN CORE								
[(PEt$_3$)(Cl)Pt.	tr	17.882(8)	70.79(2)	PtP_2ClSn	Et_3P 2.293(4)	Sn 2.524(2)	Cl,P 88,3(1,3.6)	[262]
(μ-η^2-dppm).	P$\bar{1}$	11.443(6)	88.18(2)		η^{2}P 2.316(2)		P,Sn 92.1(1,1.8)	
Fe(CO)$_3${Si(OMe)$_3$}.	2	12.457(6)	72.25(2)		Cl 2.379(2)			
SnCl$_2$]CH$_2$Cl$_2$				$SnCl_2PtFe$	Cl 2.413(3,14)	Fe 2.568(2)	Pt,Fe 115.8(1)	
(bright yellow)				FeC_3PSiSn	OC 1.787(7,8)		Si,Sn 93.9(1)	
					η^{2}P 2.261(2)		P,Sn 91.5(1)	
					Si 2.326(3)			
[{η^1-C$_6$Cl$_5$)(CNxylyl-	m	14.212/(4)		PtC_3PtHg	η^{1}C 2.06(3)	Hg 2.575(2)	C,P 94.7(9,7)	[262]
2,6)PtHg(μ-η^2-dppm).	P2$_1$/n	26.717(8)	117.58(2)		LNC 1.99(3)		C,Hg 85.4(9,2.2)	
Fe.(CO)$_3${Si(OMe)$_3$}].	4	19.318(6)			η^{2}P 2.257(9)			
CH$_2$Cl$_2$				HgPtFe		Fe 2.634(6)	Pt,Fe 164.7(2)	
(bright yellow)				FeC_3PSiHg	OC 1.69(3,7)		C,P 97.9(11,4.8)	
					η^{2}P 2.236(10)		C,Si 81.9(11,3.7)	
					Si 2.316(13)		C,Hg 76.1(15,3.7)	
							P,Hg 89.6(2)	
							Si,Hg 91.5(2)	
(PPh$_3$)$_2$(η^1-C$_6$Cl$_5$)Pt.	tr	12.122(3)	63.27(6)	PtP_2CHg	P 2.289(4,4)	Hg 2.572(1)	P,P 103.2(1)	[263]
HgW(CO)$_3$(cp)	P$\bar{1}$	13.287(6)	65.25(6)		η^{1}C 2.117(6)		P,C 91.9(2)	
(yellow)	2	18.961(17)	70.24(4)				164.8(2)	
							P,Hg 87.5(1)	
							166.4(1)	
							C,Hg 77.4 (2)	
				HgPtW		W 2.755(1)	Pt,W 171.9(1)	
				WC_8Hg	OC 1.96(2,16)		C,Hg 70.3(3,3.0)	
					η^{5}cpC 2.40(8)		132.9(3)	
[(η^4-pp$_3$)PtHg.	m	19.437(4)		Pt^6P_4Hg	η^{4}P 2.271(7,27)	Hg 2.590(2)	P,Hg 93.3(2,4.2) 175.1(2)	[264]
Mn(CO)$_5$].	P2$_1$/c	32.201(6)	94.44(2)		2.315(7,10)		Pt,Mn 176.12(12)	
Otf.1.5CH $_2$Cl$_2$^{c}.	8	17.411(4)		Hg^5PtMn		Mn 2.618(4)	C,Hg 82.8(11,3.3)	
(yellow)				MnC_5Hg	OC not given		178.20(11)	
(at 218(2) K)							P,Hg 93.3(2,1.7)	
				Pt^6P_4Hg	η^{4}P 2.276(7,40)	Hg 2.605(2)	177.7(2)	
					2.334(7,1)		Pt,Mn 178.96(14)	
				Hg^6PtMn		Mn 2.647(5)	C,Hg 84(2)	
				Mn^6C_5Hg	OC not given		176.4(11)	
[(PMe$_3$)$_2$Pt(μ-	tr	10.624(2)	75.97(2)	PtP_2CW	P 2.255(6)	W 2.771(1)	P,P 98.6(2)	[265]
CC$_6$H$_4$Me-4).	P$\bar{1}$	12.073(2)	71.52(2)		2.346(7)	C 88.4(11)	P,C 100.0(7)	
W(CO)$_4$Re(CO)$_5$].	2	15.135(3)	69.84(1)		μC 1.962(23)		160.1(6)	
0.5CH$_2$Cl$_2$							P,W 115.2(2)	
(orange)							146.2(2)	
							C,W 46.6(7)	
				WC_5PtRe	OC 2.033(30,51)	Re 3.082(1)	Pt,Re 151.3(1)	
					μC 1 2.013(24)			
				ReC_5W	OC 1.775(33,20)		C,W 85.8(13,2.4)	
							173.7(11)	
Pt(μ-η:η-C≡CSiMe$_3$)$_4$.	m	15.788(3)		PtC_5	μC 1.989(9,26)	Rh 3.0034(8)	μCμC 79.8(3)	[266]
Rh(η^4-cod).	P2$_1$/c	17.668(3)	104.47(2)		2.377(8)	Ir 3.611	92.4(3)	
Ir(η^4-cod).	4	16.229(3)			C 2.244(8)		Rh,Ir 154.16	
(orange)				RhC_8	η^{6}C not given		not given	
					μC 2.293(8,19)			
					C 2.441(9,17)			
				IrC_7	η^{6}C not given		not given	
					μC 2.238(9,39)			
					C 2.204(10)			
D: UNIQUE STRUCTURES								
(PPh$_3$)$_2$PtRu(CO)	tr	11.192(2)	83.41(1)	PtP_2CRu	P 2.288(2)	Ru 2.717(6)	P,P 101.39(6)	[267]
(cp).	P$\bar{1}$	12.520(2)	84.66(1)		2.348(2)		P,Ru 112.27(5)	
(μ$_3$-η^1:η^3:η^1-	2	22.622(4)	81.73(1)		μC 2.045(6)		146.17(4)	
CH$_2$CCPh).							μC,Ru 52.0(2)	
Au(PPh$_3$)].CF$_3$SO$_3$				RuC_9Pt	OC 1.888(7)		μCμC 37.9(2)	
(pale yellow)					η^{5}cpC not given		μC,Pt 47.8(2)	
					C 2.230(7)		77.7(2)	
					μC 2.194(7,20)			
				AuCP	μC 2.052(7)		μC,P 175.0(2)	
					P 2.233(2(			

Continued Table 9. Crystallographic and structural data for heterotrinuclear PtMM' clusters[a].

COMPOUND (colour)	Crys.cl. Sp.Grp Z	a [Å] b [Å] c [Å]	α [°] ß [°] γ [°]	Chromo-phore	M - L [Å]	M - M [Å] M – L - M [°]	L – M - L [°]	Ref
{(η^4-cod)PtSn(η^1-Bu^t)$_2$}. (μ-C_5H_4)$_2$Fe (amber)(at 173(2) K)	tr P$\bar{1}$ 2	9.948(1) 10.278(1) 13.833(2)	88.582(9) 80.205(9) 61.915(8)	PtC_5Sn SnC_3Pt FeC_{10}	η^4codC 2.246(4,18) 2.330(4,10) μC 2.034(4) Bu^tC 2.214(4,3) μC 2.163(3) C 2.041(4,16) μC 2.053(3,13)	Sn 2.6065(4) Fe 3.770(1) Fe 3.461(1)	μC,Sn 85,82(9) μC,Pt 108.74(9) not given	[268]
[I_2Cd(μ-η^2-pz)$_2$. Pt(μ-η^1:η^5-Ph_2P. C_5H_4)$_2$Fe]. 0.45CH_2Cl_2	m P2/c 8	35.376(10) 13.522(7) 19.749(8)	116.22(3)	PtN_2P_2 CdN_2I_2 FeC_{10}	$\mu\eta^2$N 2.082(9,30) $\mu\eta^1$P 2.277(3,4) $\mu\eta^2$N 2.246(10,2) I 2.732(2,16) η^5cpC not given		N,N 86.9(4) P,P 98.8(1) N,P 87.7(3,1) 169.7(3,2) N,N 88.1(3) I,I 116.26(6) N,I 112.1(3,12.9) not given	[269]
Fe(μ-η^5:η^1-$C_5H_4PPh_2$)$_2$. Pt(Cl)(μ-N)OsO_3[c] (red)	m $P2_1/c$ 8	20.058&(2) 14.899(1) 23.949(2)	114.57(2)	PtP_2NCl FeC_{10} OsO_3N PtP_2NCl FeC_{10} OsO_3N	P 2.267(5,2) μN 2.05(1) Cl 2.317(5) C not given O 1.72(2,5) μN 1.66(1) P 2.268(5,19) μN 2.06(1) Cl 2.354(6) C not given O 1.62(2,9) μN 1.65(2)	N 160.4(9) N 152(1)	P,P 99.6(2) P,μN 91.9(4) 168.1(4) P,Cl 85.0(2) 175.4(2) C,Cl 83.5(4) not given O,O 110.7(9,2.0) O,μN 108.0(9,1.6) P,P 97.7(2) P,μN 90.4(5) 171.8(5 P,Cl 87.7(2) 174.6(2) not given O,O 111(1,5) O,μN 107(1,4)	[270]
[(OC)$_4$Mo(μ-η^1:η^5-Ph_2. PC_5H_4)$_2$Ti(μ-SPh)$_2$. Pt(η^1-C_6F_5)]. 0.5PhMe.0.5$C_3H_7Pr^i$	tr P$\bar{1}$ 2	13.706(3) 14.141(3) 19.670(4)	86.63(1) 82.50(1) 65.11(1)	PtC_2S_2 $TiC_{10}S_2$ MoC_4P_2	η^1C 1.997(5,30) μS 2.256(1) 2.347(1) η^5cpC not given μS 2.305(1) 2.456(2) OC 1.898(5,69) 2.181(6,25) η^1P 2.354(1) 2.511(1)	Ti 3.014(1) S not given	C,C 87.5(2) μS,μS 101.74(4) C,μS 70.40(13) 86.44(13) not given P,P 95.27(4)	[271]

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. There are two crystallographically independent molecules.

heterotrimetllic zwitterions, formed by the binuclear anionic fragment {(cod)Ir. (μ-C≡CSiMe$_3$)(μ-C≡CSiMe$_3$) Pt(μ-C≡CSiMe$_3$)$_2$}$^-$, which in turn acts as a chelating dimetallic bidentate ligand toward the cationic {Rh(cod)}$^+$ unit. The R-Pt-Ir angle is 154.16º.

The remaining five coloured species [267-271] have unique structures (Table 9D). The crystal of the pale yellow PtRuAu complex [267] contains discrete [(PPh$_3$)$_2$PtRu(CO)(cp)(μ$_3$-η^1:η^3:η^1-CH$_2$CCPh)Au(PPh$_3$)]$^+$ cations and $CF_3SO_3^-$ anions. In the cation, a Pt-Ru bond of 2.7171(6) Å is supported by a CH_2CCPh alkyl, which is η^3-bonded to Ru and η^1-bonded to each of Pt (through the CPh carbon) and Au (through the central carbon). The Ph_3P-Au-C fragment is close to linear (175.0(2)º).

In the amber complex [268], the binuclear (η^4-cod) PtSn(η^1-Bu^t)$_2$ fragment is bridged by ferrocenophane. The Pt...Fe and Sn...Fe separations of 3.770(1) and 3.461(1) Å rule out direct metal-metal bonds. However, the Pt-Sn distance of 2.6055(4) Å is a direct bond.

In the CdPtFe complex [269], three metal centers are connected as I_2Cd(μ-η^2-pz)Pt{μ-η^1:η^5-P(Ph)$_2$C$_5$H$_4$}$_2$Fe without any metal-metal bonds. The Cd atom has a tetrahedral geometry (CdN_2I_2), Pt has square-planar geometry (PtN_2P_2) and Fe is sandwiched (FeC_{10}).

Table 10. Summary of the Pt-M bond distances in heterotrimeric platinum clusters.

Pt-M (M=non-transition)	Distances [Å] Shortest[ref]	Longest[ref]	Average	Pt-M (M=transition)	Distances [Å] Shortest[ref]	Longest[ref]	Average
Pt-Al	2.317(2)[118]	2.335(2)[118]	2.326	Pt-Co	2.4896(9)[211]	2.6197(4) [76]	2.549
Pt-Ga	2.315(1)[117]	2.382(2)[118]	2.351	Pt-Ni	2.5870(4)[76]	2.611(4)[77]	2.599
Pt-Ge	2.4345(9)[120]	2.4722(12)[120]	2.450	Pt-Fe	2.528(2)[258]	2.973(3)[184]	2.613
Pt-Sn	2.524(2)[262]	2.640(1)[129]	2.549	Pt-Os	2.647(1)[56]	2.824(2)[52]	2.697
Pt-Sb	2.491(1)[123]	2.6667(9)[116]	2.560	Pt-Pd	2.560(2)[251]	2.9365(6)[201]	2.701
Pt-In	2.556(2)[117]	2.569(2)[117]	2.562	Pt-Cu	2.519(2)[187]	2.9843(1)[89]	2.726
Pt-Li	2.537(1)[131]	2.628(7)[132]	2.582	Pt-Ru	2.609(1)[155]	2.943(8)[260]	2.729
Pt-Hg	2.572(1)[263]	2.725(2)[19]	2.658	Pt-Ir	2.618(2)[159]	2.957(1)[186]	2.733
Pt-Pb	2.701(1)[18]	2.793(2)[22]	2.738	Pt-Au	2.599(3)[154]	2.956(2)[257]	2.744
Pt-Tl	2.698(1)[16]	2.8090(7)[24]	2.770	Pt-W	2.711(1)[191]	2.883(1)[253]	2.784
Pt-Te	2.787(7)[196]	2.809(7)[196]	2.798	Pt-Re	2.731(1)[215]	2.906(1)[170]	2.812
				Pt-Ag	2.668(1)[81]	2.996(1)[203]	2.829
				Pt-Mn	2.6644(15)[76]	2.9995(18)[76]	2.862
				Pt-Mo	2.707(1)[53]	3.001(1)[9]	2.890

Table 11. Summary of the M-M and M-M' bond distances in heterotrimeric platinum clusters.

Pt-M (M=non-transition)	Distances [Å] Shortest[ref]	Longest[ref]	Average	Pt-M (M=transition)	Distances [Å] Shortest[ref]	Longest[ref]	Average
Mo-Mo	2.094(1)[209]	2.1023(9)[209]	2.097	Co-Pd	2.537(3)[251]		
Co-Co	2.372(2)[152]	2.533(2)[150]	2.351	Fe-Sn	2.568(4)[262]		
V-V	2.556(2)[181]			Rh-Mo	2.619(1)[255]		
Fe-Fe	2.484(7)[176]	2.802(5)[184]	2.565	Mn-Hg	2.618(4)[264]	2.647(5)[264]	2.632
Rh-Rh	2.641(1)[173]	2.667(9)[116]	2.652	Fe-Hg	2.634(6)[262]		
Pt-Pt	2.581(1)[38]	2.969(1)[25]	2.706	Cu-W	2.648(2)[254]		
Mn-Mn	2.638(2)[183]	2.8154(14)[132]	2.726	Fe-Mn	2.676(3)[259]	2.692(3)[259]	2.684
Au-Au	2.673(2)[158]	2.888(1)[185]	2.747	Fe-Ru	2.639(3)[258]	2.761(2)[258]	2.700
Ir-Ir	2.7551(12)[116]	2.7681(13)[130]	2.761	Fe-W	2.694(2)[253]	2.784(3)[253]	2.735
Sb-Sb	2.7551(12)[116]	2.7681(13)[130]	2.761	W-Hg	2.755(1)[263]		
Ru-Ru	2.725(1)[165]	2.86614)[164]	2.808	W-Au	2.763(2)[256]	2.801(2)[257]	2.782
Os-Os	2.860(2)[162]	2.916(4)[163]	2.880	Mn-Re	2.8216(13)[261]		
Ag-Ag	2.906(1)[24]			Ti-Ru	2.836(2)[260]		

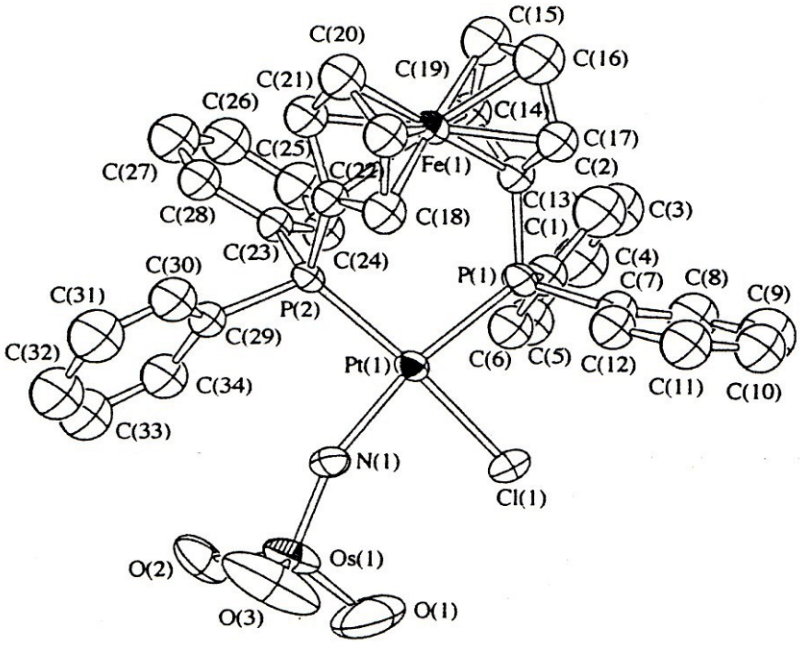

Figure 16. Structure of Fe(μ-η^5:η^1-$C_5H_4PPh_2$)$_2$Pt(Cl)μ-N)OsO_3 [270].

The structure of one of the two crystallographically independent molecules in the unit cell of Fe(μ-η^5:η^1-$C_5H_4PPh_2)_2$Pt(Cl)(μ-N)OsO_3 [270] is shown in Fig. 16. The geometry around Pt is square planar. Interestingly, the Pt-N≡Os linkage is slightly bent with an average angle of ca. 156.2º. This bending is attributed to the non-bonding repulsion between the $NOsO_3$ group and the phenyl ring of dppf.

Another trinuclear complex [271] displays a Mo-Ti-Pt bent chain (angle 169.1º) in which the Mo... Ti and Ti...Pt pairs are connected by a double cyclopentadienylphosphine and benzenethiolate bridging system. The central Ti(IV) atom lies in a pseudo-tetrahedral environment involving the two π-cyclopentadienyl rings from the two cyclopenta-dienyldiphenylphosphine ligands and the two sulfur atoms of the thiolate groups. The sulfur atoms are bonded to the Pt(II) center, which completes its distorted square-planar coordination with the C_{ipso} atoms of the two C_6F_5 groups mutually cis. Finally, the Mo(0) atom is octahedrally coordinated, being bound to four CO ligands and to two P atoms from the two $C_5H_4PPh_2$ groups.

Inspection of the data in Table 9 reveals that the shortest Pt-M and M-M' bond distances are 2.524(2) Å for Pt-Sn [262] and 2.537(3) Å for Co-Pd [251]. There are three derivatives [259,264,270] which contain two crystallographically independent molecules that differ mostly by degree of distortion and are additional examples of distortion isomerism [37].

5. Conclusions

This review includes over three hundred and sixty heterotrimeric platinum clusters with compositions Pt_2M (205 examples), PtM_2 (132 examples) and PtMM' (24 examples). The heterometals include the non-transition and transition metals.

The heterotrimetallic Pt clusters exist in six different crystal classes: monoclinic, triclinic, orthorhombic, tetragonal, trigonal and rhombohedral. The first two are by far the most common with 189 examples (monoclinic) and 122 examples (triclinic). The remaining four have 37 examples (or), 10 examples (tg), 2 examples (trg) and one example (rh).

Three metal atoms form a wide variety of frameworks: M_3 triangular, dicapped M_3 triangle, M_3 of V shape, five-, six- or seven- membered metallocycles, M_3 linear and unique structures. This results in a rich chemistry of platinum not only from the variety of metals, but also from their framework and stereochemistry. A triangular and a linear framework are the most common. The mean values of the Pt-M and Pt-Pt bonds found in triangular frameworks (Pt_2M, PtM_2, PtMM'; M are non-transition metals) are 2.692 and 2.770Å. The average deviation value from the ideal angle (60°) is 6°. The mean values of the respective triangular frameworks when M is a transition metal are: 2.695 and 2.848Å. In the series of M_3 linear arrays, the mean values of the Pt-M, M-M as well as of the respective (Pt-M-Pt, M-Pt-M, Pt-M-M') angles are 2.660, 2.644Å and 162.7°, when M is a non-

transition metal; and 2.730, 2.747Å and 172.8° when M is a transition metal.

A summary of the Pt-M bond distances in the heterotrimeric derivatives is given in Table 10. The Pt-M (non-transition) and Pt-M (transition) bonds are given in increasing order of the average Pt-M bond distances. The shortest Pt-M (non-transition) and Pt-M (transition) bonds are 2.315(1) Å for Pt-Ga [117] and 2.4896(9) Å for the Pt-Co bond [211].

A summary of the M-M and M-M' bond distances is given in Table 11, where the shortest are 2.094(1) Å for Mo-Mo [209] and 2.537(3) Å for Co-Pd [251]. The shortest Pt-Pt bond distance is 2.581(1) Å [38].

There are two derivatives [51,111] which exist in two isomeric forms that differ only by degree of distortion. Seventeen derivatives [19,31,76,80,85, 107,118,148,214,224,231,239,241,244,259,264,270] contain two crystallographically independent molecules differing by degree of distortion in the M-L distances and L-M-L angles. In $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$ [176], four such molecules are present. Such examples are typical of the general class of distortion isomerism [37].

Platinum complexes are important both from a chemical and biological point of view, and structural information is important for the understanding of their role in both areas. This represents the first overview of structural data for heterotrimeric platinum derivatives. We are also preparing structural reviews in heterotetra and heterooligomeric platinum clusters. Despite the increasing use of data retrieval systems, the tracing of relevant material is not always straightforward. Some relevant data are not available and structural features of comparative interest can often be overlooked. In addition, some publications use differing names for ligands and do not indicate bridge donor atoms, and sometimes use differing atom numbering schemes. It is hoped that this review will serve to draw together common structural threads and stimulate activity in areas of particular interest.

Abbreviations

ac	acetate;
acac	acetylacetonate;
aet	2-aminoethanethiolate;
betmp	bis(ethythio)methylenepropanedioate;
bpen	1,8-bis(phenylethynyl)naphthalene;
bpvcp	2,2´-bipyridine-4-vinylcyclopentadienyl;
bpy	2,2-bipoyridine;
Bu^t	tert-butyl;
Bu^t_2bpy	4,4´-di-tert-butyl-2.2´-bipyridine;
$C_{23}H_{11}$	$C{\equiv}C\text{-}C_6H_5\text{-}C_6H_3\text{-}C{\equiv}C$;
C_6Cl_5	pentachlorophenyl;
C_6F_5	pentafluorophenyl;
C_6H_{14}	hexyne;
C_6H_6	benzene;
C_7H_{16}	heptane;
can	cantharidinate;
$CC_6H_4Me\text{-}4$	4-tolylidyne;
cod	cycloocta-1,5-diene;
cp	cyclopentadienyl;
cp*	pentamethylcyclopentadienyl;
daedt	2,2-diacetyl-1,1-ethylenedithiolate;
dach	1,2-diaminocyclohexane;
dcp	dicyclopentadiene;
dcpe	bis(dicyclohexylphosphino)ethane;
dcptp	$C_5H_4S\text{-}(CH_2)_3\text{-}SC_5H_4$;
dhpe	1,2-diphosphinoethane;
dmamp	2,6-bis((dimethylamino)methyl)phenyl;
dmat	$Me_2NCH_2C_5H_4$;

dmcyt	1,5-dimethylcytosinate;
dmdb	7,9-dimethyl-7,9-$C_2B_{10}H_{10}$;
dmg	dimethylglyoximate;
dmpe	1,2-bis(dimethylphosphino)ethane;
dmpNC	2,6-dimethylphenylisocyanide;
docp	$C_{12}H_8O_2$;
dpae	2,6-$Pr^i_2C_6H_3N$=C(Me)C(Me)=NC_6H_3 Pr^i_2-2,6;
dpbpy	3,3´bis(diphenylphosphino)-2,2´-bipyridine;
dpmp	bis((diphenylphosphino)metyl)phenylphosphine;
dpmpd	$Ph_2CH_2P(Ph)CH_2P(Ph)_2C(CO_2Me)C(CO_2Me)$;
dpmpe	$Ph_2CH_2P(Ph)CH_2P(Ph)_2CHC(CO_2Et)$;
dpmpm	$Ph_2CH_2P(Ph)CH_2P(Ph)_2CHC(CO_2Me)$;
dppa	bis(diphenylphosphino)amine;
dppe	1,2-bis(diphenylphosphine)ethane;
dppen	1,2-bis(diphenylphosphine)ethene;
dpphen	2,9-bis(diphenylphosphino)-1,10-phenanthroline;
dppm	bis(diphenylphosphino)methane;
dppp	1,3-bis(diphenylphosphino)propane;
dpppp	$Ph_2P(CH_2)_3P(Ph)C_6H_4$-o;
dppy	2,6-bis(diphenylphosphino)pyridine;
dtbpe	1,2-bis(di-tert-butylphosphine)ethane;
edt	1,1-ethylenedithioalate;
en	ethylenediamine;
Et	ethyl;
Et_2NCS_2	N,N-diethyldithiocarbamate;
$F_3CC_2CF_3$	hexafluorobut-2-yne;
$HB(pz)_3$	hydrotris(pyrazol-1-yl)borate;
chy_3P	tri(cyclohepta-2,4,6-trienyl)phosphine;
m	monoclinic;
Mal	MeO_2CCH=$CHCO_2Me$;
Me	methyl;
Me_4en	N,N,N´,N´-tetramethylethylenediamine;
mec	1-methylcytosinate;
MeC≡CMe	dimethylacetylene;
2,9-Me_2phen	2,9-dimethyl-1,10-phenanthroline;
4-Mepy	4-methylpyridine;
mes	mesityl(2,4,6-trimethylphenyl);
mesNC	mesitylisocyanide;
met	1-methylthyminate;
meu	1-methyluracilate;
mnt	maleonitriledithioalate;
mtp	$Ph_2P(S)CH_2$;
nphpcp	naphtalenephenylphosphinecyclopentadienyl;
(np)$PhPC_5H_4$	1-naphthylphenylphosphinocyclopentadienyl;
obet	ortho-C≡CC_6H_4C≡CC_6H_4C≡C-ortho;
or	orthorhombic;
pap	(2-pyridylamino)phenyl;
PBu_3	tributylphosphine;
p-Bupy	p-butylpyridine;
Pcy_2	dicyclohexylphosphide;
Pcy_3	tricycloheylphosphine;
pen	d-penicillaminate;
PEt_3	triethylphosphine;

Ph	phenyl;
Ph_2pyP	diphenylpyridine-2-phosphine;
phb	phenylborole;
PhC≡CC≡CPh	1,4-diphenylbut-1,3-diine;
PhC≡CPh	diphenylacetylene;
phen	1,10-phenanthroline;
Pmdeta	N,N,N',N",N"-pentamethyldiethyletriamine;
PMe_2Ph	dimethylphenylphosphine;
PMe_3	trimethylphosphine;
$PMeBu^t_2$	di-tert-butylmethylphosphine;
$PMePh_2$	diphenylmethylphosphine;
1,2-pn	1,2-diaminopropane;
$POPh_2$	diphenylphosphinite;
PPh_2	diphenylphosphide;
PPh_3	triphenylphosphine;
$Pr^i_2NCS_2$	N,N-diisopropyldithiocarbamate;
$PSPh_2$	diphenylthiophosphinite;
ptd	4-phenyl-1,2.4-triazoline-3,5-dione;
py	pyridine;
pycp	pyridinecyclopentadienyl;
pycp*	2-pyridyltetramethylcyclopentadienyl;
pyo	2-pyridonate;
pyphos	6-(diphenylphosphino-2-pyridonate);
pz	pyrazol-1-yl;
$pz(b_2:d_2)$	7,8;17,18-dibenzophorphyrazinate-2,3,12,13-tetraphosphinate;
rh	rhombohedral;
SPh	thiophenyl;
sqo	silsesquioxane;
temdb	1,3,4,5-tetraethyl-2,3-dihydro-2-methyl-14-1,3-diborolyl;
tg	tetragonal;
thf	tetrahydrofuran;
tht	tetrahydrothiophene;
tmen	N,N,N',N"-tetramethylethylenediamine;
tol	toluene;
tolpy	(2-pyridylamino)toluenyl;
tr	triclinic;
trg	trigonal;
triphos	bis[2-(dophenylphosphino)ethyl]phenylphosphine;
xylNC	2,6-xylylisocyanide.

References

[1] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 22, 263 (2002)

[2] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 23, 125 (2003)

[3] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 24, 135 (2004)

[4] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 24, 301 (2004)

[5] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 25, 93 (2005)

[6] M. Melník, C.E. Holloway, Coord. Chem. Rev. 250, 2261 (2006)

[7] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 32, 23 (2012)

[8] C.E. Holloway, M. Melník, Rev. Inorg. Chem. 32, 111 (2012)

[9] C.E. Holloway, M. Melník, Centr. Eur. J. Chem. 9, 501 (2011)

[10] M. Melník, O. Sprušanský, C.E. Holloway, Centr. Eur. J. Chem. 10, 1709 (2012)

[11] M.C. Janzen, M.C. Jennings, R.J. Puddephatt, Organometallics 20, 4100 (2001)
[12] M.E. Cucciolito, F. Giordano, F. Ruffo, V. De Felice, J. Organomet. Chem. 503, 251 (1995)
[13] Tanase, H. Ukaji, Y. Kudo, M. Ohno, K. Kobayashi, Y. Yamamoto, Organometallics 13, 1374 (1994)
[14] T. Taase, Y. Yamamoto, R.J. Pudephatt, Organometallics 15, 1502 (1996)
[15] G.P.C.M. Dekker, C.J. Elsevier, S.N. Poelsma, K. Vrieze, P.W.N.M. van Leeuwen, W.J.J. Smeets, A.L. Spek, Inorg. Chim. Acta 195, 203 (1992)
[16] R. Uson, J. Forniés, M. Tomás, R. Garde, P.J. Alonso, J. Amer. Chem. Soc. 117, 1837 (1995)
[17] P.R. Sharp, Inorg. Chem. 25, 4185 (1986)
[18] J.M. Casas, J. Forniés, A. Marlin, V.M. Orera, A.G. Orpen, A.J. Rueda, Inorg. Chem. 34, 6514 (1995)
[19] D.V. Toronto, A.L. Balch, Inorg. Chem. 33, 6132 (1994)
[20] R. Usón, J. Forniés, L.R. Falvello, I. Ara, I. Usón, Inorg. Chim. Acta, 212, 105 (1993)
[21] V.J. Catalano, B.L. Bennett, B.C. Noll, Chem. Commun. 1413 (2000)
[22] R. Usón, J. Forniés, L.R. Falvello, M.A. Usón, I. Usón, Inorg. Chem. 31, 3697 (1992)
[23] V.J. Catalano, B.L. Bennett, R.L. Yson, B.C. Noll, J. Amer. Chem. Soc. 122, 10056 (2000)
[24] Hai-Bin Song, Zhing-Zhi Zhang, Zheng Hui, Chi-Ming Che, T.C.W. Mak, Inorg. Chem. 41, 3146 (2002)
[25] (a) W. Li, Ch.L. Barnbes, P.R. Sharp, J. Chem. Soc., Chem. Commun. 1634 (1990); (b) J.J. Li, W. Li, P.R. Sharp, Inorg. Chem. 35, 604 (1996)
[26] M. Zhou, Y. Xu, C.-F. Lam, P.-H. Leung, L.-L. Koh, K.F. Mok, T.S.A. Hor, Inorg. Chem. 33, 1572 (1994)
[27] M. Zhou, Y. Xu, L.-L. Koh, K.F. Mok, P.-H. Leung, T.S.A. Hor, Inorg. Chem. 32, 1875 (1993)
[28] S.W.A. Fong, W.T. Yap, J.J. Vittal, T.S.A. Hor, W. Henderson, A.G. Oliver, C.E.F. Rickard, J. Chem. Soc., Dalton Trans. 1986 (2001)
[29] Meisheng Zhou, Yan Xu, Choon-Fui Lam, Lin Koh, K.F. Mok, Pak-Hing Leung, T.S.A. Hor, Inorg. Chem. 32, 4660 (1993)
[30] M.S. Zhou, A.T. Tan, Y. Xu, C.-F. Lam, P.-H. Leung, K.F. Mok, L.-L. Koh, T.S.A. Hor, Polyhedron 16, 2381 (1997)
[31] Zh. Li, Zh.-H. Loh, S.W.A. Fong, Y.-K. Yan, W. Henderson, K.F. Mok, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 1027 (2000)
[32] Zh. Li, X. Xu, S. B. Khoo, K.F. Mok, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 2901 (2000)
[33] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 315 (2001)
[34] J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 328 (2002)
[35] J.C. Poat, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, Polyhedron 11, 2125 (1992)
[36] Y.-H. Wang, Zh.-X. Huang, G. Wu, Polyhedron 16, 57 (1997)
[37] M. Melník, Coord. Chem. Rev. 47, 239 (1982)
[38] P. Braunstein, J.L. Richert, Y. Dusausoy, J. Chem. Soc., Dalton Trans. 3801 (1990)
[39] R. Bender, P. Braunstein, B. Metz, P. Lemoine, Organometallics 3, 381 (1984)
[40] R. Bender, P. Braunstein, S.E. Braund, D. Rouag, P.D. Harvey, S. Golhen, L. Ouahab, Inorg. Chem. 41, 1739 (2002)
[41] C. Archambault, R. Bender, P. Braunstein, Y. Dusausoy, J. Chem. Soc., Dalton Trans. 4084 (2002)
[42] V.G. Albano, G. Ciani, J. Organomet. Chem. 66, 311 (1974)
[43] (a) G.J. Arsenault, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, I. Traurnicht, Angew. Chem. Int. Ed. Engl. 26, 86 (1987); (b) L. Manojlovič-Muir, K.W. Muir, I. Treurnicht, R.J. Puddephatt, Inorg. Chem. 26, 2418 (1987)
[44] C.M. Hill, D.M. Mingos, H. Powell, M.J. Watson, J. Organomet. Chem. 441, 499 (1992)
[45] A. Modinos, P. Woodward, J. Chem. Soc., Dalton Trans. 1534 (1975)
[46] M.I. Bruce, J.G. Matisons, B.W. Skelton, A.H. White, Aust. J. Chem. 35, 687 (1982)
[47] (a) M.I. Bruce, M.R. Snow, E.R.T. Tiekink, Aust. J. Chem. 39, 2145 (1986); (b) C. Archambault, R. Bender, P. Braunstein, S.E. Braund, D.Rouag, S. Golhen, L. Ouahab, Chem. Commun. 849 (2001)
[48] Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton, L.R. Falvello, R. Llusar, Organometallics 7, 2279 (1988)
[49] J.M. Casas, J. Forniés, A. Martin, B. Menjón, M. Tomás, Polyhedron 15, 3599 (1996)
[50] R. Usón, J. Forniés, M. Tomás, J .M. Casas, F.A. Cotton, LR. Falvello, J. Amer. Chem. Soc. 107, 2556 (1985)
[51] H. Liu, A.L. Tan, K.F. Mok, T.C.W. Mak, A.S. Batsanov, J.A.K. Howard, T.S.A. Hor, J. Amer. Chem. Soc. 119, 11006 (1997)
[52] V.A. Maksakov, V.P. Kirin, A.V. Virovets, S.V. Tkachev, V.I. Alekseev, N.V. Podberezskaya, J. Organomet. Chem. 539, 27 (1997)
[53] N. Carr, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, M.J. Went, Organometallics 12, 4350 (1993)
[54] (a) T.V. Ashworth, M. Berry, J.A.K. Howard,

M. Laguna, F.G.A. Stone, J. Chem. Soc., Dalton Trans. 1615 (1980); (b) T.V. Ashworth, M. Berry, J.A.K. Howard, M. Laguna, F.G.A. Stone, J. Chem. Soc., Chem. Commun. 45 (1997)
[55] (a) C. Graiff, A. Ienco, C. Massera, C. Mealli, G. Predieri, A. Tiripicchio, F. U gozzoli, Inorg. Chim. Acta 330, 95 (2002); (b) K. Panneerselvam, T.H.Lu, S.F. Tung, A.K. Dash, P. Mathur, Acta Crystallogr., Sect. C 55, 1250 (1999)
[56] R.D. Adams, U. Bunz, B. Captain, W. Fu, W. Steffen, J. Organomet. Chem. 614-615, 75 (2000)
[57] S. Yamazaki, A.J. Deeming, D.M. Speel, Organometallics 17, 775 (1998)
[58] (a) T. Tanase, H. Ukaji, H. Takahata, H .Toda, T. Igoshi, Y. Yamamoto, Organometallics 17, 196 (1998); (b) T. Tanase, H. Takahata, H. Ukaji, M. Savegawa, Y. Yamamoto, J. Organomet. Chem. 538, 247 (1997)
[59] L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 162 (1981)
[60] R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton, L.R. Falvello, Inorg. Chem. 26, 3482 (1987)
[61] M.J. Chetcuti, K. Marsden, I. Moore, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 1749 (1982)
[62] M. Gorzellik, B. Nuber, T. Bohn, M.L. Ziegler, J. Organomet. Chem. 429, 173 (1992)
[63] J.M. Casas, L.R. Falvello, J. Forniés, A. Martin, Inorg. Chem. 35 7867 (1996)
[64] N. Hadj-Bagheri, R.J. Puddephatt, Inorg. Chim. Acta 213 29 (1993)
[65] M.F. Hallam, M.A. Luke, D.M.P. Mingos, I.D. Williams, J. Organomet. Chem. 325, 271 (1987)
[66] H. Liu, A.L. Tan, Y. Xu, K.F. Mok, T.S.A. Hor, Polyhedron 16, 377 (1997)
[67] D.I. Gilmour, M.A. Luke, D.M.P. Mingos, J. Chem. Soc., Dalton Trans. 335 (1987)
[68] C.E. Briant, D.I. Gilmour, M.A. Luke, D.M.P. Mingos, J. Chem. Soc., Dalton Trans. 851 (1985)
[69] H. Liu, A.L. Tau, K.F. Mok, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 4023 (1996)
[70] Z. Li, H. Liu, K.F. Mok, A.S. Batsanov, J.A.K. Howard, T.S.A. Hor, J. Organomet. Chem. 575, 223 (1999)
[71] H. Liu, C. Jiang, J.S.L. Yeo, K.F. Mok, L.K. Liu, T.S.A. Hor, Y.K. Yan, J. Organomet. Chem. 595, 276 (2000)
[72] S.W. Audi Fong, J.J. Vittal, W. Henderson, T.S.A. Hor, A.G. Oliver, C.E.F. Rickard, Chem. Commun. 421 (2001)
[73] S.W. Audi Fong, W.T. Yap, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc., Dalton Trans. 1826 (2002)
[74] W. Bos, J.J. Bour, P.P.J. Schlebos, P. Hageman, W.P. Bosman, J.M.M. Smits, J.A.C. van Wietmarschen, P.T. Beurskens, Inorg. Chim. Acta 119, 141 (1986)
[75] Z. Li, Z.H. Loh, K.F. Mok, T.S.A. Hor, Inorg. Chem. 39, 5299 (2000)
[76] W. Chen, K. Matsumoto, Eur. J. Inorg. Chem. 2664 (2002)
[77] A. Erxleben, A. Albinati, B. Lippert, J. Chem. Soc., Dalton Trans. 1823 (1996)
[78] A. Schreiber, O. Krizanovic, E.C. Fusch, B. Lippert, F. Lianza, A. Albinati, S. Hill, D.M.L. Goodgame, H. Stratemeier, M.A. Hitchman, Inorg. Chem. 33, 6101 (1994)
[79] W. Micklitz, G. Müller, J. Riede, B. Lippert, J. Chem. Soc., Chem. Commun. 76 (1987)
[80] W. Micklitz, G. Müller, B. Huber, J. Riede, F. Rashvau, J. Heinze, B. Lippert, J. Amer. Chem. Soc. 110, 7084 (1988)
[81] J. Forniés, R. Navarro, M. Tomás, E.P. Urriolabeitia, Organometallics 12, 940 (1993)
[82] B. Lippert, U. Thewalt, H. Schöllhorn, D.M.L. Goodgame, R.W. Rollins, Inorg. Chem. 23, 2807 (1984)
[83] I. Mutikainen, O. Orama, A. Pajunen, B. Lippert, Inorg. Chim. Acta 137, 189 (1987)
[84] B. Lippert, U. Schubert, Inorg. Chim. Acta 56, 15 (1981)
[85] R. Usón, J. Forniés, L.R. Falvello, M. Tomás, J.M. Casas, A. Martin, Inorg. Chem. 32, 5212 (1993)
[86] (a) A. Albinati, F. Demartin, L.M. Venanzi, M.K. Wolfer, Angew. Chem. Int. Ed. Engl. 27, 563 (1988); (b) A. Albinati, S. Chaloupka, F. Demartin, T.F. Koetzke, H. Rüegger, L.M. Venanzi, M.K. Wolfer, J. Amer. Chem. Soc. 115, 169 (1993)
[87] B. Lippert, D. Neugebauer, Inorg. Chim. Acta 46, 171 (1980)
[88] V.G. Albano, M.Di Serio, M . Monari, I. Orabona, A. Panunzi, F. Ruffo, Inorg. Chem. 41, 2672 (2002)
[89] G. Frommer, F. Lianza, A. Albinati, B. Lippert, Inorg. Chem. 31, 2434 (1992)
[90] T. Tanase, R.A. Begum, Organometallics 20, 106 (2001)
[91] Y. Yamamoto, T. Tanase, H. Ukaji, M. Haseguwa, T. Igoshi, K. Yoshimura, J. Organomet. Chem. 498, C23 (1995)
[92] T. Tanase, H. Toda, K. Kobarjashi, Y. Yamamoto, Organometallics 15, 5272 (1996)
[93] T. Tanase, R.A. Begum, H. Toda, Y. Yamamoto,

Organometallics 20, 968 (2001)
[94] T. Tanase, H. Toda, Y. Yamamoto, Inorg. Chem. 36, 1571 (1997)
[95] W.V. Konze, V.G. Young, Jr., R.J. Angelici, Organometallics 18, 258 (1999)
[96] S. Schecht, J. Magull, D. Fenske, K. Dehnicke, Angew. Chem. Int. Ed. Engl. 36, 1994 (1997)
[97] S. Yamazaki, A.J. Deeming, J. Chem. Soc., Dalton Trans. 3051 (1993)
[98] I. Ara, J.R. Berenguer, J. Forniés, E. Lalinde, M.T. Moreno, J. Organomet. Chem. 510, 63 (1996)
[99] E. Alonso, J. Forniés, C. Fortúno, M. Tomás, J. Chem. Soc., Dalton Trans. 3777 (1995)
[100] (a) J.R. Aclan, G.H.W. Milburn, L. Sawyer, V.K. Shaf, T.A. Stephenson, P.M. Veitch, Acta Crystallogr., Sect. C 41, 58 (1985); (b) R.E. Marsh, Acta Crystallogr., Sect. C 41, 1383 (1985)
[101] D.M. Anderson, A.J. Blake, J.D. Fotheringham, T.A. Stephenson, J.R. Allan, P.M. Weitch, Acta Crystallogr., Sect. C 44, 1305 (1988)
[102] J.R. Berenguer, E. Eguizábal, L.R. Falvello, J. Forniés, E. Lalinde, A. Martin, Organometallics 19, 490 (2000)
[103] I.M. Kim, J.S. Park, Y.-S. Kim, Y.J. Jun, T.Y. Kang, Y.S. Sohn, M.J. Jun, Angew. Chem. Int. Ed. Engl. 40, 2458 (2001)
[104] J. Vicente, M .T. Chicote, S. Huertas, P.J. Jones, A.K. Fischer, Inorg. Chem. 40, 6193 (2001)
[105] J.W. Sibert, T.F. Baumann, D.J. Williams, A.J.P. White, A.G.M. Barrett, B.M. Hoffman, J. Amer. Chem. Soc. 118, 10487 (1996)
[106] T. Yoshida, T. Shinohara, K. Onitsuka, F. Osawa, K. Sonogashira, J. Organomet. Chem. 574, 66 (1999)
[107] T. Yoshida, S. Tanaka, T. Adachi, T. Yoshida, K. Onitsuka, K. Sonogashira, Angew. Chem. Int. Ed. Engl. 34, 319 (1995)
[108] K. Onitsuka, T. Yoshida, A. Ichimura, T. Adachi, T. Yoshida,, K. Sonogashira, Chem. Lett. 427 (1995)
[109] B. Neumann, U. Siemeling, H.G. Stammler, U. Vorfield, J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F.F. de Biani, P. Zanello,J. Chem. Soc., Dalton Trans. 4705 (1997)
[110] J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, N. Veldman, A.L. Spek, J. Fraanje, K. Goubitz, J. Organomet. Chem. 514, 125 (1996)
[111] P.R. Ranatunge-Bandarage, N.W. Duffy, S.M. Johnston, B.H. Robinson, K. Simpson, Organometallics, 13, 511 (1994)
[112] C.E.L. Headford, R. Mason, P.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, J. Chem. Soc., Chem. Commun. 601 (1990)
[113] N.J. Long, A.J. Martin, R. Vilar, A.J.P. White, D.J. Williams, M. Younus, Organometallics 18, 4261 (1999)
[114] W. Henderson, S.R. Alley, Inorg. Chim. Acta 322, 106 (2001)
[115] Wui-Yeung Wong, Wai-Kunk Wong, P.R. Raithby, J. Chem. Soc., Dalton Trans. 2761 (1998)
[116] S.J. Black, D.E. Hibbs, M.B. Hursthouse, C. Jones, J.W. Steed, Chem. Commun., 2199 (1998)
[117] D. Weiss, M. Winter, K. Merz, A. Knüfer, R.A. Fischer, N. Fröhlich, G. Funking, Polyhedron 21, 535 (2002)
[118] D. Weiss, T. Steinke, M. Winter, R.A. Fischer, N. Fröhlich, J. Uddin, G. Frenking, Organometallics 19, 4583 (2000)
[119] N .W. Alcock, J.H. Nelson, J. Chem. Soc., Dalton Trans. 2415 (1982)
[120] K. Mochida, T. Wada, K. Suzuki, W. Hatanaka, Y. Nishiyama, M. Nanjo, A. Sekine, Y. Ohashi, M. Sakamoto, A. Yamamoto, Bull. Chem. Soc. Jpn. 74, 123 (2001)
[121] E.N. Yurchenko, T.S. Khodashova, M.A. Porai-Koshits, V.P. Mel'nikova, V.F. Brattsev, Koord. Khim. 11, 359 (1985); Engl. Ed. 11, 195 (1985)
[122] J.H. Nelson, W.L. Wilson, L.W. Cary, N.W. Alcock, H.J. Clase, G.S. Jas, L. Ramsey-Tassin, J.W. Kenney, III., Inorg. Chem. 35, 883 (1996)
[123] O.F. Wendt, A. Scodinu, L.I. Elding, Inorg. Chim. Acta 277, 237 (1998)
[124] P. Sharma, A. Cabrera, M. Sharma, C. Alvarez, J.L. Arias, R.M. Gomez, S. Hernandez, Z. Anorg. Allg. Chem. 626, 2330 (2000)
[125] G.W. Bushnell, D.T. Eadic, A. Pidcock, A.R. Sam, R.D. Holmes-Smith, S.R. Stobart, E.T. Brennan, T.S. Cameron, J. Amer. Chem. Soc. 104, 5837 (1982)
[126] L. Wesemann, S. Hagen, T. marx, I. Pantenburg, M. Nobis, B. Driessen-Hölscher, Eur. J. Inorg. Chem. 2261 (2002)
[127] U. Baumeister, H. Hartung, T. Schulz, H. Weichmann, Acta Crystallogr., Sect. C 54, 333 (1998)
[128] Y. Obora, Y. Tsuji, K. Nishiyama, M. Ebihara, T. Kavamura, J. Amer. Chem. Soc. 118, 10922 (1996)
[129] T. Marx, L. Wasemann, S. Dehnen, I. Pantenburg, Chem. Eur. J. 7, 3025 (2001)
[130] S.J. Black, D.E. Hibbs, M.B. Hursthouse, C. Jones, K.M.A. Malik, R.C. Thomas, J. Chem.

Soc., Dalton Trans. 4321 (1997)
[131] R. Wyrwa, H.O. Fröhlich, H. Görls, Z. Anorg. Allg. Chem. 626, 819 (2000)
[132] H.O. Fröhlich, R. Wyrwa, H. Görls, U. Pieper, J. Organomet. Chem. 471, 23 (1994)
[133] H.O. Fröhlich, R. Wyrwa, H. Görls, Angew. Chem. Int. Ed. Engl. 32, 387 (1993)
[134] A. Albinati, P.S. Pregosini, H. Rüegger, Inorg. Chem. 23, 3223 (1984)
[135] L.M. Rendina, J.J. Vittal, R.J. Puddephatt, Organometallics 15, 1749 (1996)
[136] M.C. Janzen, H.A. Jenkins, L.M. Rendina, J.J. Vittal, R.J. Puddephatt, Inorg. Chem. 38, 2123 (1999)
[137] M.C. Janzen, H.A. Jenkins, M.C. Jennings, L.M. Rendina, R.J. Puddephatt, J. Chem. Soc., Dalton Trans., (1999) 1713; Organometallics 21, 1257 (2002)
[138] H. Grützmacher, H. Pritzkow, Chem. Ber. 126, 2409 (1993)
[139] H. Gilges, U. Schubert, Eur. J. Inorg. Chem. 897 (1998)
[140] U. Baumeister, H. Hartung, A. Krug, K. Merzweiler, T. Schulz, C. Wagner, H. Weichmann, Z. Anorg. Allg. Chem. 626, 2185 (2000)
[141] U. Kohler, H.D. Hausen, J. Weidlein, J. Organomet. Chem. 272 (1984) 337.
[142] R.M. Barr, M. Goldstein, T. Nigel, D. Hairs, M. McPartlin, A.J. Marwell, J. Chem. Soc., Chem. Commun. 221 (1974)
[143] T.F. Carlson, J.P. Fackler, Jr., R.J. Staples, R.E.P. Wimpenny, Inorg. Chem. 34, 426 (1995)
[144] D. Zhang, D.B. McConville, C.A. Tessier, W.J. Youngs, Organometallics 16, 824 (1997)
[145] J.P.H. Charmant, L.R. Falvello, J. Forniés, J. Gómez, E. Lalinde, M.T. Moreno, A.G. Orpen, A. Rueda, Chem. Commun. 2045 (1999)
[146] E.A. Quadrelli, J.E. Davies, B.F.G. Johnson, N. Feeder, Chem. Commun. 1031 (2000)
[147] R.D. Adams, G. Chen, W. Wu, J. Yin, Inorg. Chem. 29, 4208 (1990)
[148] I. Bachert, I. Bartusseck, P. Barunstein, E. Guillon, J. Rosé, G. Kickelbick, J. Organomet. Chem. 580, 257 (1999)
[149] R. Bender, P. Branstein, J. Fischer, L. Ricard, A. Mitschler, Nouv. J. Chim. 5, 81 (1981)
[150] M. Breuer, J. Strähle, Z. Anorg. Allg. Chem. 619, 1564 (1993)
[151] L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, R.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 1134 (1981)
[152] P .D. Macklin, C.A. Mirkin, N. Viswanathan, G.A. Williams, G.L. Geoffroy, A.L. Rheingold, J. Organomet. Chem. 334, 117 (1987)
[153] R. Mason, J.A. Zubieta, J. Organomet. Chem. 66, 289 (1974)
[154] P. Braunstein, H. Lehner, D.Matt, A. Tiripicchio, M. Tiripicchio-Camellini, Angew. Chem. Int. Ed. Engl. 23, 304 (1984)
[155] D.L. Davies, J.C. Jeffery, D. Miguel, P. Sherwood, F.G.A. Stone, J. Organomet. Chem. 383, 463 (1990)
[156] A.B. Antonova, S.V. Kovalenko, A.A. Ioganson, N.A. Deikhina, E.D. Korniets, Y.T. Struchkov, Y.L. Slovokhotov, A.I. Yanovskii, A.G. Ginzburg, P.V. Petrovskii, Metalloorg. Khim. 2, 1090 (1989) (In Russian); Engl. Ed., p. 575
[157] R. Bender, P. Braunstein, J.L. Richert, Y. Dusausoy, New. J. Chem. 14, 569 (1990)
[158] B.T. Sterenberg, H.A. Jenkins, R.J. Puddephatt, Organometallics 18, 219 (1999)
[159] (a) N.M. Boag, M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone, P. Woodward, J. Chem. Soc., Chem. Commun. 1171 (1980); (b) M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 1309 (1982)
[160] S.I.Al-Resayes, P.B. Hitckock, M.F. Meidine, J.F. Nixon, J. Organomet. Chem. 341, 457 (1988)
[161] P. Sundberg, J. Chem. Soc., Chem. Commun. 1307 (1987)
[162] R.D. Adams, G. Chen, J.Ch. Lii, W. Wu, Inorg. Chem. 30, 1007 (1990)
[163] J. Cooke, R.E.D. McClung, J. Takats, R.D. Rogers, Organometallics 15, 4459 (1996)
[164] R.D. Adams, G. Chen, W. Wu, J. Cluster Sci. 4 119 (1993)
[165] R.D. Adams, W. Wu, Organometallics 12, 1248 (1993)
[166] (a) M. Green, J.A.K. Howard, R.M. Mills, G.N. Pain, F.G.A. Stone, P. Woodward, J. Chem. Soc., Chem. Commun. 869 (19881); (b) M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 1321 (1982)
[167] J. Powell, J.C. Brewer, G. Gulia, J.F. Sawyer, Inorg. Chem. 28, 4470 (1989)
[168] J. Powell, J.C. Brewer, G. Gulia, J.F. Sawyer, J. Chem. Soc., Dalton Trans. 2503 (1992)
[169] P. Antognazza, T., Beringhelli, G. D'Alfonso, A. Minoja, G. Ciani, M. Moret, A. Sironi, Organometallics 11, 1777 (1992)
[170] T Beringhelli, A. Ceriotti, G. D'Alfonso, R.D. Pergolla, G. Ciani, M. Moret, A. Sironi, Organometallics 9, 1053 (1990)
[171] P. Braunstein, E. de Jesüs, A. Dedieu, M. Lanfranchi, A. Tiripicchio, Inorg. Chem. 31, 399 (1992)

[172] L. Weber, I. Schumann, H.G. Stammler, B. Neumann, Chem. Ber. 127, 1349 (1994)
[173] R.S. Dickson, G.D. Fallon, K.D. Heazle, M.J. Liddell, J. Organomet. Chem. 430, 221 (1992)
[174] P. Blenkiron, G.D. Enright, A.J. Carty, Chem. Commun. 483 (1997)
[175] S.I. Al-Resayes, P.B. Hitchocock, J.F. Nixon, J. Chem. Soc., Chem. Commun. 928 (1987)
[176] A.A. Pasynskii, B.I. Kolobkov, S.E. Nefedov, I.L. Eremenko, E.S. Koltun, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 454, 229 (1993)
[177] A. Morneau, W.E. Geiger, M.G. Richmond, M.J. Don, W.H. Watson, A. Nagl, Organometallics 21, 1247 (2002)
[178] (a) A.A. Pasynskii, N.I. Semenova, Yu. T. Torubaev, P.V. Belousov, K.A. Lyssenko, Zh.V. Dobrokhotova, Izv. Akad. Nauk, Sec. Khim. 11, 2115 (2001) (in Russian); (b) A.A. Pasynskii, N.I. Semenova, Yu. T. Torubaev, P.V. Belousov, K.A. Lyssenko, Zh.V. Dobrokhotova, Russ. Chem. Bult., Inter. Ed. 50, 2215 (2001)
[179] (a) A.A. Pasynskii, N.I. Semenova, Yu.V. Torubaev, K.A. Lysenko, Zh. Neorg. Khim. 46, 1981 (2001) (in Russian), Engl. Ed., p. 1807; (b) M. Capdevilla, Y. Carasso, W. Clegg, R.A. Coxall, P. Gonzáles-Duaite, A. Lledós, J.A. Ramiréz, J. Chem. Soc., Dalton Trans. 3103 (1999)
[180] V.W. Day, D.A. Lesch, T.B. Rauchfus, J. Amer. Chem. Soc. 104, 1290 (1982)
[181] C.M. Bolinger, T.B. Rauchfuss, S.R. Wilson, J. Amer. Chem. Soc. 106, 7800 (1984)
[182] W.H. Watson, A. Nagl, M.J. Don, M.G. Richmond, J. Chem. Crystallogr. 30, 33 (2000)
[183] R.D. Adams, O.S. Kwong, M.D. Smith, Inorg. Chem. 41, 1658 (2002)
[184] A.M. Mazany, J.P. Fackler, Jr., M.K. Gallgher, D. Seyferth, Inorg. Chem. 22, 2593 (1983)
[185] D. Maseri, T. Kochi, Z. Tang, Y. Ishii, Y. Mozobe, M. Hidai, J. Organomet. Chem. 620, 69 (2001)
[186] P.A. Shapley, H.Ch. Liang, M.C. Dopke, Organometallics 20, 4700 (2001)
[187] A. Hegmans, E. Zangrando, E. Freisinger, F. Pichierri, L. Randaccio, C. Mealli, M. Gerdan, A.X. Trautwein, B. Lippert, Chem. Eur. J. 5, 3010 (1999)
[188] D. Moras, J. Dehand, R. Weiss, C.R. Acad. Sc. Paris, Ser. C 267, 1471 (1968)
[189] P. Braunstein, G. Predieri, F.J. Lahoz, A. Tiripicchio, J. Organomet. Chem. 288, C13(1985)
[190] H.H. Murray, D.A. Briggs, G. Garzón, R.G. Raptis, L.C. Porter, J.P. Fackler, Jr., Organometallics 6, 1992 (1987)
[191] T.V. Ashworth, M.J. Chetcuti, J.A.K. Howard, F.G.A. Stone, S.J. Wisbey, P. Woodward, J. Chem. Soc., Dalton Trans. 763 (1981)
[192] S.H.F. Becke, M.D. Bermúdez, N.H. Tran-.Huy, J.A.K. Howard, O. Johnson, F.G.A. Stone, J. Chem. Soc., Dalton Trans. 1229 (1987)
[193] P. Braunstein, D. Matt, O. Bars, D. Grandjean, Angew. Chem. Int. Ed. Engl. 18, 797 (1979)
[194] (a) P. Braunstein, D. Matt, O. Bars, M. Louer, D. Grandjean, J. Fischer, A. Mitschler, J. Organomet. Chem. 213, 79 (1981); (b) T. Blum, P. Braunstein, A. Tiripicchio, M. Tiripicchio-Camellini, Organometallics 8, 2504 (1989)
[195] P. Braunstein, U. Englert, G.E. Herberick, M. Neuschütz, M.U. Schmidt, J. Chem. Soc., Dalton Trans. 2807 (1999)
[196] J.C. Daran, B. Meunier, K. Prout, Acta Crystallogr., Sect. B 35, 1709 (1979)
[197] (a) E. Kunz, J. Müller, U. Schubert, J. Organomet. Chem. 320, C11 (1987); (b) E. Kunz, M. Knorr, J. Willnecker, U. Schubert, New J. Chem. 12, 467 (1988)
[198] M.A. Urbancic, S.R. Wilson, J.R. Shapley, Inorg. Chem. 23, 2954 (1984)
[199] Ch. King, D.D. Heinrich, G. Garzón, Je-Ch. Wang, J.P. Fackler, Jr., J. Amer. Chem. Soc. 111, 2300 (1989)
[200] Braunstein, E. Keller, H. Vahrenkamp, J. Organomet. Chem. 165, 233 (1979)
[201] D. Holthenrich, E. Zangrando, E. Chiarparin, B. Lippert, L. Randaccio, J. Chem. Soc., Dalton Trans. 4407 (1997)
[202] J. Forniés, E. Lalinde, A. Martin, M.T. Moreno, J. Organomet. Chem. 490, 179 (1995)
[203] M. Ebihara, M. Tsuchiya, M. Yamada, K. Tokoro, T. Kawamura, Inorg. Chim. Acta, 231 (1995) 35.
[204] I. Ara, J.R. Berenguer, J. Forniés, E. Lalinde, Inorg. Chim. Acta 264, 199 (1997)
[205] H. Honda, T. Yoshimura, M. Hirtosu, T. Kawamoto, T. Konno, Inorg. Chem. 41, 2229 (2002)
[206] Y. Yamada, Y. Miyashita, K. Fujisawa, K. Okamoto, Bull. Chem. Soc. Jpn. 75, 1151 (2002)
[207] A. Castellanos, J.J. Garcia, H. Torrens, N. Bailey, D.O.R. de Barbarin, A. Gurtierrez and F. del Rio, J. Chem. Soc., Dalton Trans. 2861 (1994)
[208] V. Wing-Wah Yam, L.-P. Chan, T.-F. Lai, J. Chem. Soc., Dalton Trans. 2075 (1993)
[209] H. Nakano, A. Nakamura, K. Mashima, Inorg. Chem. 35, 4007 (1996)

[210] (a) R.D. Adams, Wei Fu, Bo Qu, J. Cluster Sc. 11, 55 (2000); (b) D. Holthenrich, M. Krumm, E. Zangrando, F. Pichierri, L. Randaccio, B. Lippert, J. Chem. Soc., Dalton Trans. 3275 (1995)
[211] S. Back, R.A. Gossage, M. Lutz, I. del Rio, A.L. Spek, H. Lang, G. van Koten, Organometallics 19, 3296 (2000)
[212] Th. Fässler, G. Huttner, J. Organomet. Chem. 381, 391 (1990)
[213] P. Mattur, Md. M. Hossain, K. Das, U.C. Sinha, J. Chem. Soc., Chem. Commun. 46 (1993)
[214] S. Kuwata, Y. Mizobe, M. Hidai, J. Amer. Chem. Soc. 115, 8499 (1993)
[215] T. Weidmann, V. Weinrich, B. Wagner, Ch. Robl, W. Beck, Chem. Ber. 124, 1363 (1991)
[216] I. Ara, J. Forniés, E. Lalinde, M.T. Moreno, M. Tomás, J. Chem. Soc., Dalton Trans. (27351994)
[217] I. Ara, J.R. Berenguez, E. Eguizábal, J. Forniés, E. Lalinde, F. Martinez, Organometallics 18, 4344 (1999)
[218] (a) Wa-Hung Leung, J.L.C. Chim, Wing-Tak Wong, J. Chem. Soc., Dalton Trans. 3153 (1996); (b) W.-H. Leung, J.L.C. Chim, W.-T. Wong, J. Chem. Soc., Dalton Trans. 3277 (1997)
[219] S. Schwarz, J. Strähle, Z. Anorg. Allg. Chem. 628, 2795 (2002)
[220] S. Schwarz, J. Strähle, Z. Anorg. Allg. Chem. 628, 1556 (2002)
[221] R. Usón, J. Forniés, M. Tomás, I. Ara, J.M. Casas, Polyhedron 11, 1783 (1992)
[222] R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton, L.R. Falvello, Inorg. Chem. 25, 4519 (1986)
[223] E.A.V. Ebsworth, R.O. Gould, N.T. McManus, D.W.H. Rankin, M.D. Walkinshaw and J.D. Whitelock, J. Organomet. Chem. 249, 227 (1983)
[224] A.J. Deeming, B.R. Cockerton, S. Doherty, Polyhedron 16, 1945 (1997)
[225] A.J. Deeming, S. Doherty, Polyhedron 15, 1175 (1996)
[226] G.N. Richardson, U. Brand, H. Vahrenkamp, Inorg. Chem. 38, 3070 (1999)
[227] P. Braunstein, G.E. Herberich, M. Neuschütz, M.U. Schmidt, J. Organomet. Chem. 580, 66 (1999)
[228] M. Zhou, B.W. Pfenning, J. Steiger, D. van Engen, A.B. Bocarsky, Inorg. Chem. 29, 2456 (1990)
[229] R. Podgajny, Y. Dromzeé, K. Kruczaha, B. Sieklucka, Polyhedron 20, 685 (2001)
[230] H. Wadelpohl, H. Pritzkov, W. Siebert, Chem. Ber. 118, 729 (1985)
[231] M.I. Bruce, B.C. Hall, P.J. Low, M.E. Smith, B.W. Skalton, A.H. White, Inorg. Chim. Acta, 300-302, 633 (2000)
[232] M. Sato, H. Anano, J. Organomet. Chem. 555, 167 (1998)
[233] U. Nettckoven, M. Widhalm, P.C.J. Kaner, P.W.N.M. van Leeuwen, K. Mereiter, M. Lutz, A.L. Spek, Organometallics 19, 2299 (2000)
[234] O. Carugo, G. De Santis, L. Fabbrizzi, M. Licchelli, A. Monichino, P. Pallavicini, Inorg. Chem. 31, 765 (1992)
[235] K. Jacob, F. Voigt, K. Merzweiler, C. Pietzsch, J. Organomet. Chem. 545-546, 421 (1997)
[236] R.E. Hollands, A.G. Osborne, R.H. Whiteley, Ch.J. Cardin, J. Chem. Soc., Dalton Trans. 1527 (1985)
[237] W. Weigand, Ch. Robl, Chem. Ber. 126, 1807 (1993)
[238] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 641, 173 (2002)
[239] A.O. Larsen, B.A. Taylor, P.S. White, M.R. Cagné, Organometallics 18, 5157 (1999)
[240] S. Achar, Ch.E. Immoos, M.G. Hill, V.J. Catalano, Inorg. Chem. 36, 2114 (1997)
[241] C.J. Adam, E.J. Blackie, J.L. Morgan, S.A. Mole, B.H. Robinson, J. Simpson, J. Chem. Soc., Dalton Trans. 2362 (2001)
[242] N.J. Long, A.J.P. White, D.J. Williams, M. Younus, J. Organomet. Chem. 649, 94 (2002)
[243] S. Otto, A. Roodt, Acta Crystallogr., Sect. C 53, 1414 (1997)
[244] P. Štěpnička, J. Podlaha, R. Gyepes, M. Polášek, J. Organomet. Chem. 552, 293 (1998)
[245] T. Mizuta, T. Yamasaki, K. Miyoshi, Chem. Letters 924 (2000)
[246] L. Manojlovič-Muir, A.N. Henderson, I. Treurnicht, R.J. Puddephatt, Organometallics, 8, 2055 (1989)
[247] E. Fritsch, K. Polborn, Ch. Robl, K. Sünkel, W. Beck, Z. Anorg. Allg. Chem. 619, 2050 (1993)
[248] M. Di Vaird, P. Stoppione, Polyhedron 13, 3045 (1994)
[249] J. Müller, E. Zangrando, N. Pahlke, E. Freisinger, L. Randaccio, B. Lippert, Chem. Eur. J. 4, 397 (1998)
[250] (a) J. Forniés, M.A. Usón, J.I. Gil, P.G. Jones, J. Organomet. Chem. 311, 243 (1986); (b) P.G. Jones, J. Organomet. Chem. 345, 405 (1988)
[251] P. Braunstein, C. de Bellefon, Y. Dusausoy, D. Bayeul, J. Cluster Sc. 6, 175 (1995)
[252] M. Chetcuti, M. Green, J.A.K. Howard,

J.C. Jeffery, R.M. Mills, G.N. Pain, S.J. Porter, F.G.A. Stone, A.A. Wilson, P. Woodward, J. Chem. Soc., Chem. Commun. 1057 (1980)
[253] M.J. Chetcuti, J.A.K. Howard, R.M. Mills, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. 1757 (1982)
[254] G.A. Carriedo, J.A.K. Howard, F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1984) 1555; J. Organomet. Chem. 250, C28 (1983)
[255] L.J. Farrugia, A.D. Miles, F.G.A. Stone, J. Chem. Soc., Dalton Trans. 2451 (1984)
[256] T. Blum, P. Braunstein, A. Tiripicchio, M. Tiripicchio-Camellini, New J. Chem. 12, 539 (1988)
[257] G.A. Carriedo, J.A.K. Howard, F.G.A. Stone, M.J. Went, J. Chem. Soc., Dalton Trans. 2545 (1984)
[258] R.R. Willis, C.E. Schuchart, A. Wojcicki, A.L. Rheingold, B.S. Haggerty, Organometallics 19, 3179 (2000)
[259] A.B. Antonova, A.A. Johansson, N.A. Deykhina, D.A. Pogrebnyakov, N.I. Pavlenko, A.I. Rubaylo, F.M. Dolgushin, P.V. Petrovskii, A.G. Ginzburg, J. Organomet. Chem. 577, 238 (1999)
[260] S. Kuwata, S. Kobashima, N. Sergiyama, Y. Ishii, M. Hidai, Inorg. Chem. 40, 2034 (2001)
[261] D. Miguel, D. Morales, V. Riera, S. Garcia-Granda, Angew. Chem. Int. Ed. Engl. 41, 3034 (2002)
[262] P. Braunstein, M. Knorr, M. Stramfer, A. Tiripicchio, F. Ugozzoli, Organometallics 13, 3038 (1994)
[263] P. Braunstein, O. Rossell, M. Seco, I. Torra, X. Solans, C. Miravitlles, Organometallics 5, 1113 (1986)
[264] W. Schuh, H. Kopacka, K. Wurst, P. Peringer, Eur. J. Inorg. Chem. 2399 (2001)
[265] J.C. Jeffery, D.B. Lewis, G.E. Lewis, M.J. Parrott, F.G.A. Stone, J. Chem. Soc., Dalton Trans. 1717 (1986)
[266] I. Ara, J.R. Berenguer, E. Eguizábal, J. Forniés, E. Lalinde, Organometallics 20, 2686 (2001)
[267] R.R. Willis, M. Calligaris, P. Faleschini, A. Wojcicki, J. Clust. Sci. 11, 233 (2000)
[268] F. Jälke, R. Rulkens, G. Zech, D.A. Foucher, A.J. Lough, I. Manners, Chem. Eur. J. 4, 2117 (1998)
[269] C. Pettinari, F. Marchetti, A. Cingolani, S.I. Troyanov, A. Drozdov, J. Chem. Soc., Dalton Trans. 3335 (1998)
[270] W.-H. Leung, J.L.C. Chim, W.-T. Wong, J. Chem. Soc., Dalton Trans. 3277 (1997)
[271] I. Ara, E. Delgado, J. Forniés, E. Hernández, E. Lalinde, N. Mansilla, M.T. Moreno, J. Chem. Soc., Dalton Trans. 3201 (1996)