DOI 10.1515/mgmc-2012-0037 — Main Group Met. Chem. 2012; 35(5-6): 117–127

Review

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Structural characterisation of heterometallic platinum complexes with non-transition metals. Part I: heterodimeric complexes

Abstract: This review covers 90 heterodimeric Pt complexes with non-transition metals. There are 13 non-transition metals (Ge, Sn, Pb, Ga, In, Tl, Sb, Zn, Cd, Hg, Na, K and Ca). These dimers can be divided into three groups, the first in which only a direct Pt-M bond connects respective units (59%); the second in which in additon to a direct Pt-M bond a ligand/s serves as bridge/s (33%); and the third one in which two respective units are held together via bridge/s ligand/s. The mean Pt-M bond distance elongates in the sequence: 2.425 Å (M=Ge) <2.559 Å (Sb) <2.601 Å (In) <2.625 Å (Cd) <2.657 Å (Hg) <2.663 Å (Sn) <2.670 Å (Pb) <2.674 Å (Tl) <2.760 Å (Zn) <2.960 Å (Ca). The Pt atom has oxidation numbers 0, +2 (most common) and +4, and the M atoms have +1, +2 (most common), +3 and +4. The Pt coordination geometrics include square planar (most common), trigonal bipyramidal, pseudo-octahedral Pt(IV). There are examples which contain two independent dimers (distortion isomers). Factors affecting bond distances and angles are discussed and some ambiguities in coordination polyhedra are outlined.

Keywords: non-transition metal; platinum heterodimers; structure; trans effect.

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List of abbreviations

ac	acetate
bpy	2,2′-bipyridyl
4,4′-Bu^t_2bpy	di(4,4′-terc-butyl)-2,2′-bipyridyl
C_4Me_4	tetramethylcyclobutadiene
C_6F_5	pentafluorophenyl
cy	cyclohexyl
damp	2-(dimethylaminomethyl)phenyl
dcpe	$cy_2PCH_2CH_2Pcy_2$
dmso	dimethylsulphoxide
dpb	1,3-diisopropyl-benzo-1,3.2-diazaborolidine
dppe	(1,2-diphenylphosphino)amine
dppp	bis(2-diphenylphosphophenyl)phosphane
Me	methyl
Me_2ann	8-dimethylamino-1-naphthyl
Me_2phen	2,9-dimethyl-1,10-phenanthroline
mpt	CH_2-C_6H_4-P(o-tolyl)$_2$
npe	CH_2CMe_3
PEt_3	triethylphoshine
Ph	phenyl
phen	1,10-phenathroline
Ph_2PthqH	diphenylphosphine hydroquinolinate
PMe_2Ph	dimethylphenylphosphine
pp_3	tris(2-diphenylphosphophenyl)phosphane
pz_3BH	tris(pyrazol-1-yl)borate

Introduction

The past 50 years have seen many studies on the reaction of various metal salts. In many cases, heterometal compounds have been obtained for which crystallographic and structural data could be obtained. Heterometallic compounds form a fascinating and rapidly growing branch of chemistry that it can be called ‘polyhedral cluster chemistry’. The key role in theoretical and practical behaviours of the clusters is played by the metal-metal bond as well as non-bond opening and closing. It is interesting that ‘cooperation’ in heterometallics between transition metals is much more frequent than heterometallics between transition and non-transition metal atoms. The aim of this paper is to analyse and classify heterodimeric PtM complexes, where M are non-transition metals.

Heterodimeric PtM complexes

PtM (M=Ge, Sn or Pb) complexes

There are 15 such complexes, which can be divided into two groups, one in which PtL_n and GeL_n units are held together only by a direct Pt-Ge bond, and in the other group, in addition to a direct Pt-Ge bond, is a bridging ligand. In two yellow monoclinic derivatives (Albano et al., 1999; Janzen et al., 2001), two moieties, Pt(η²-4,4′-Bu^t_2bpy)$(Me)_2Cl$ and $GeCl_3$ (Janzen et al., 2001), Pt(η²-Me_2phen)(η²-$CH{=}CH_2$)Cl and $Ge(Ph)_2Cl$ (Albano et al., 1999), are held together only by a Pt-Ge bond with lengths of 2.352(2) and 2.364(1) Å, respectively. Each Pt(IV) is hexa-PtN_2C_2ClGe (Albano et al., 1999; Janzen et al., 2001) and Ge(II) a tetrahedrally, $GeCl_3Pt$ (Janzen et al., 2001) and GeC_2ClPt (Albano et al., 1999), coordinated. In another six PtGe derivatives, two moieties: $Pt(PEt_3)_2$ and $Ge[N(SiMe_3)_2]_2$ (Figure 1) (Litz et al., 1995); $Pt(PEt_3)_2(Ph)$ and $Ge(Ph)_2(OH)$ (Gee and Powell, 1971), $Pt(PMe_2Ph)(L)$ and $Ge(Ph)_3$ [L=Et (Hasebe et al., 2000) or Me (Ozawa et al., 1998)]; $Pt(PPh_3)_2(L)$ and $Ge(CL)_3$, [L=H and CL=Ph (Habereder and Nith, 2003) η¹-dpe and Me (Habereder and Nith, 2003)] are connected only by Pt-Ge bond.

The Pt-Ge bond length elongated in the order: 2.4197(9) Å (Litz et al., 1995) <2.432(2) Å (Gee and Powell, 1971) <2.437(1) Å (Hasebe et al., 2000) <2.440(4) Å (Habereder and Nith, 2003) <2.4495(7) Å (Ozawa et al., 1998) <2.470(1) Å (Habereder and Nith, 2003). Whereas in Litz et al. (1995) both metal atoms are three-coordinated, PtP_2Ge (distorted T shape) and GeN_2Pt (distorted Y shape) in remainders are four-coordinated, PtP_2XGe [X=C (Gee and Powell, 1971; Ozawa et al., 1998; Hasebe et al., 2000), H (Habereder and Nith, 2003) or B (Habereder and Nith, 2003)] (a square-planar), GeC_2OPt (Gee and Powell, 1971) and GeC_3Pt (Ozawa et al., 1998; Hasebe et al., 2000; Habereder and Nith 2003) (a tetrahedral).

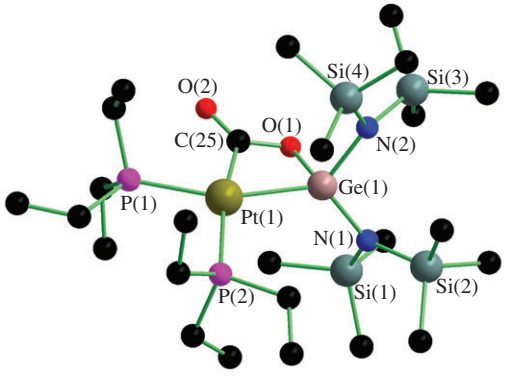

Figure 1 Structure of $[Pt(PEt_3)_2(\mu\text{-}COO)Ge\{N(SiMe_3)_2\}_2]$ (Litz et al., 1995).

There are six PtGe derivatives, in which in addition to a direct Pt-Ge bond between $Pt(PEt_3)_2$ and $Ge[N(SiMe_3)_2]_2$ units a bidentate non-chelating ligand; μ-η²-C(O)O via C atom to Pt and via O atom to Ge (Litz et al., 1995), μ-η²-N(Ph)O via N to Pt and via O to Ge (Litz et al., 1998), μ-η²-CH_2O via C to Pt and via O to Ge (Litz et al., 2000), μ-η²-N(Ph)C(O)N(Ph)O via N to Pt and via O to Ge (Litz et al., 1998), μ-η²-$S(O)_2N(Ph)O$, via S to Pt and via O to Ge (Litz et al., 1998), and μ-η²-$OCH_2N(Ph)O$ via O to Pt and via other O to Ge (Litz et al., 1998). The Pt-Ge bond length elongated in the sequence: 2.4197(9) Å (Litz et al., 1995) <2.4214(7) Å (Litz et al., 1998) <2.4368(3) Å (Litz et al., 2000) <2.4562(5) Å (Litz et al., 1998) <2.4715(11) Å (Litz et al., 1998) <2.4874(9) Å (Litz et al., 1998). Each Pt(II) atom is four-PtP_2XGe [X=C (Litz et al., 1995, 2000), N (Litz et al., 1998), S (Litz et al., 1998) or O (Litz et al., 1998)] (a distorted square planar) and Ge(II) atom also four-GeN_2OPt (Litz et al., 1995, 1998) (a tetrahedral) coordinated. The Pt-Ge bond length in the heterodimeric PtGe complexes range from 2.352(1) Å (Janzen et al., 2001) to 2.4874(9) Å (Litz et al., 1998) with a mean value of 2.432 Å. The mean Pt(II)-L bond distance elongated in the sequence: 2.11 Å (CL) <2.14 Å (BL) <2.30 Å (PL) <2.32 Å (bi-PL). It is noticeable that on the mean Pt(II)-P bond distance, there is an influence of the trans-donor atom as expected, and the distance elongated in the order: 2.30 Å (trans to P) <2.33 Å (trans to C) <2.37 Å (trans to N) ~2.37 Å (trans to S) <2.38 Å (trans to B) <2.385 Å (trans to O). The mean Ge(II)-L bond distance elongated in the sequence: 1.84 Å (OL) <1.895 Å (NL) <1.97 Å (CL) <2.20 Å (Cl). The bidentate non-chelating ligands, which serve as bridge between metal atoms, with the donor sites: C + O, N + O, S + O and O + O; all coordinated to Ge(II) atom via O atom, with mean Ge(II)-O bond distance of 1.86 Å. The mean Pt(II)-L (bridge) bond length elongated in the sequence: 2.095 Å (L=C) <2.10 Å (N) <2.105 Å (O) <2.32 Å (S). In the examples with these bridging ligands, electronic and steric factors both play a role in the resultant geometry and is reflected in the L-Pt-Ge ring angles of the respective bimetallocycles. The mean L-Pt-Ge angle opens in the order: 65.4° (CPtGeO) <66.0° (NPtGeO) <76.5° (NPtGeOC) <77.0° (OPtGeON) <82.3° (SPtGeON).

There are 30 heterodimeric PtSn derivatives, for which structural parameters are available. Structure of triclinic derivative (Nelson et al., 1996) consists of well-separated PPh_3Bz^+ cations and $[Br_3PtSnBr_3]^{-2}$ anion. Two moieties, $PtBr_3$ and $SnBr_3$, are connected via a direct Pt-Sn bond [2.486(5) Å]. The Pt(II) atom has a square-planar ($PtBr_3Sn$) and Ge(II) atom a tetrahedral ($SnBr_3Pt$)

environment. There are several other PtSn derivatives in which two units: Pt(η¹-L)(PEt_3)Cl and $SnCl_3$ [L=bao-N (Goel et al., 1981), p-Claniline-N (Albinati et al., 1985a)]; Pt(η²-dppe)Cl and $SnCl_3$ (Dahlenburg and Martel, 2001); Pt(PPh_3)$_2$H and $Sn(Ph)_3$ (Latif et al., 1994); Pt(PPh_3)$_2$H and $SnCl_3$ (Gomez et al., 1991); Pt(PPh_3)$_2$Cl and $SnCl_3$ (Cavinata et al., 1994); Pt(η²-dppp)I and $SnCl_3$ (Farkas et al., 1996); Pt(PPh_3)$_2$(η¹-$BNMe_2$) and $Sn(Me)_3$ (Habereder and Nith, 2003); Pt(PPh_3)$_2$(η¹-dpb) and $Sn(Me)_3$ (Habereder and Nith, 2003); Pt(PEt_3)$_2$(η¹-COPh) and $SnCl_3$ (Albinati et al., 1985b) are held together via a direct Pt-Sn bond. Structure of Pt(p-Clan)(PEt_3)Cl$SnCl_3$ (Albinati et al., 1985a) is shown in Figure 2.

The Pt-Sn bond lengths elongated in the order: 2.501(1) Å (Goel et al., 1981) <2.504(1) Å (Albinati et al., 1985a) <2.562(2) Å (Dahlenburg and Martel, 2001) <2.564(1) Å (Latif et al., 1994) <2.572(2) Å (Dahlenburg and Martel, 2001) <2.590 Å (Cavinata et al., 1994) <2.601(1) Å (Gomez et al., 1991) <2.611(1) Å (Farkas et al., 1996) <2.615(1) Å (Farkas et al., 1996) <2.6289(6) Å (Habereder and Nith, 2003) <2.6339(4) Å (Habereder and Nith, 2003) <2.634(1) Å (Albinati et al., 1985b). Each Pt(II) atom has a square-planar geometry [PtNClPSn (Goel et al., 1981; Albinati et al., 1985a)], PtP_2XSn [X=Cl (Cavinata et al., 1994; Dahlenburg and Martel, 2001), H (Gomez et al., 1991; Latif et al., 1994), B (Habereder and Nith, 2003), I (Farkas et al., 1996) or C (Albinati et al., 1985b)] and each Ge(II) atom has a tetrahedral geometry [SnC_3Pt (Latif et al., 1994; Habereder and Nith, 2003), $SnCl_3Pt$ (Goel et al., 1981; Albinati et al., 1985a,b; Gomez et al., 1991; Cavinata et al., 1994; Farkas et al., 1996; Dahlenburg and Martel, 2001)].

Another five PtSn dimers, each contain Sn(η⁵-$B_{11}H_{11}$) unit (Marx and Wesermann, 2000; Marx et al., 2001a,b) and with Pt(PEt_3)$_2$($CNBu^t$) (Marx et al., 2001a), Pt(Ph_3P)($CNBu^t$)[η¹-C(Ph)$NHBu^t$] (Marx et al., 2001b), Pt(η²-dppe)[η¹-C(Ph)$NHBu^t$] (Marx et al., 2001b), Pt(η³-triphos) (Marx et al., 2001a) or Pt(PPh_3)$_2$(Ph) (Marx and Wesermann, 2000) units are also connected via a direct Pt-Sn bond

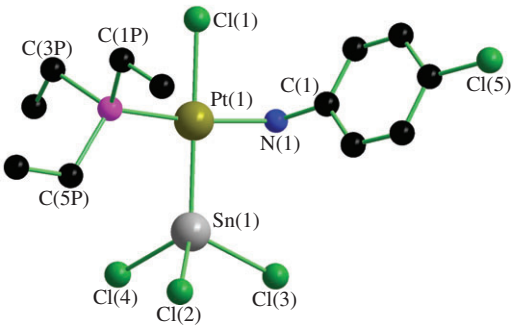

Figure 2 Structure of Pt(p-Clan)(PEt_3)Cl$SnCl_3$ (Albinati et al., 1985a).

with lengths elongated in the order: 2.590(1) Å (Marx et al., 2001a) <2.595(1) Å (Marx et al., 2001b) <2.601(1) Å (Marx et al., 2001b) <2.626(1) Å (Marx et al., 2001a) <2.651(1) Å (Marx and Wesermann, 2000). Each Pt(II) atom has a square-planar environment [PtP_2CSn (Marx and Wesermann, 2000; Marx et al., 2001a,b), PtC_3Sn (Marx et al., 2001a) and PtC_2PSn (Marx et al., 2001b)], each Sn(II) atom is five-SnB_5-coordinated. In two PtSn derivatives in which two units, Pt(η³-C_4H_7)(CO) with $SnCl_3$ (Grassi et al., 1989), Pt(η⁴-pp_3) with $SnCl_3$ (Fernandez et al., 2002), are also connected only via Pt-Sn bond [2.5496(7) and 2.574(1) Å], respectively, have Pt(II) atoms five-PtC_4Sn (Grassi et al., 1989), PtP_4Sn (Fernandez et al., 2002) coordinated. Each Sn(II) atom is tetrahedrally ($SnCl_3Pt$) coordinated. In another two PtSn dimers (Albano et al., 1992, 1996), each Pt(II) atom has an unsymmetrically tetragonal bipyramid environment (PtN_2C_2ClSn) with Cl and Sn atom at axial positions and Sn(II) atoms are tetrahedrally coordinated (SnC_2ClPt). In both dimers, two units Pt(η²-2,9-Me_2phen)(η²-CH_2=CH_2)Cl with $Sn(Ph)_2Cl$ (Albano et al., 1992); Pt(η²-2,9-Me_2phen)(η²-MeO_2CCH=$CHCO_2Me$)Cl with $Sn(Me)_2Cl$ (Albano et al., 1996) are held together only via a direct Pt-Sn bond [2.534(1) and 2.5864(7) Å], respectively.

There are eight Pt(IV)Sn(II) dimers (Rüegger et al., 1988; Smeets et al., 1992; Levy et al., 1996a,b; Canty et al., 1999; Marx et al., 2000; Janzen et al., 2001) in which two non-equivalent units: Pt(η²-4,4′-Bu^t_2bpy)$(Me)_2$Cl with $SnCl_3$ or $SnCl_2$(Ph) (Janzen et al., 2001); Pt[η³-$CH_2C(Me)CH_2$](η²-styrene) with $SnCl_3$ (Rüegger et al., 1988); Pt(η²-4,4′-Bu^t_2bpy)$(Me)_2$ with $Sn(Me)_2Cl$ (Levy et al., 1996a); Pt(η²-4,4′-Bu^t_2bpy$(Me)_2$I with $Sn(Me)_3$ (Levy et al., 1996b); Pt(η²-Me_2ann)$_2$Cl with $SnCl_3$ (Smeets et al., 1992); Pt(η²-4,4′-Bu^t_2bpy)(Ph)($CNBu^t$)(Bz) with Sn(η⁵-$B_{11}H_{11}$) (Marx et al., 2000) and Pt(η³-pz_3BH)$(Me)_2$ with $Sn(Me)_3$ (Canty et al., 1999) are connected only via a direct Pt(IV)-Sn(II) bond, which elongated in the order: 2.4932(7) Å (Janzen et al., 2001) <2.5186(6) Å (Janzen et al., 2001) <2.5393(7) Å (Rüegger et al., 1988) <2.541(2) Å (Levy et al., 1996a) <2.547(5) Å (Levy et al., 1996b) <2.5489(5) Å (Smeets et al., 1992) <2.554(1) Å (Marx et al., 2000) <2.567(4) Å (Levy et al., 1996b) <2.5727(8) Å (Canty et al., 1999). In Levy et al. (1996a), the Pt(IV) atom is five-(PtN_2C_2Sn) coordinated and in remainders six-PtN_2C_2XSn [X=Cl (Smeets et al., 1992; Janzen et al., 2001) or I (Levy et al., 1996b)], PtC_5Sn (Rüegger et al., 1988), PtC_3N_2Sn (Marx et al., 2000) and PtN_3C_2Sn (Canty et al., 1999) coordinated. The Sn(II) atom is found with the chromophores: $SnCl_3Pt$ (Rüegger et al., 1988; Smeets et al., 1992; Janzen et al., 2001), SnC_2ClPt (Levy et al., 1996a; Janzen et al., 2001), SnC_3Pt (Levy et al., 1996b; Canty et al., 1999) and SnB_5Pt (Marx et al., 2000). In yellow Pt(IV)Sn(II) dimer (Janzen et al., 1999,

2002), two units Pt(η^2-4,4′-Bu$^t_2$bpy)(Me)$_2$ with Sn(Me)$_2$ are held together via a direct Pt-Sn bond [2.5578(7) Å] and heterobidentate non-chelating μ-η^2-SeC(CO$_2$Me)=C(CO$_2$Me) ligand via Se to Pt(IV) and via C to Sn(II). The Pt(IV) has a pseudo-octahedral PtN$_2$C$_2$SeSn and Sn(II) atom tetrahedral SnC$_3$Pt coordination.

In pale yellow Pt(II)Sn(II) dimer (Figure 3) (Carr et al., 1983), two units Pt(PPh$_3$)$_2$ and Sn(Ph)$_3$ are held together by C atom, of S(C)S(Me) ligand with Pt-C-Sn bridge angle of 122.2(8)°. In addition, one S atom of the ligand coordinated to Pt(II) atom and created a three-membered ring [μC-Pt-S, 48.5(5)°]. Each metal atom is four-coordinated (PtP$_2$CS, SnC$_4$).

The mean Pt(II)-L bond distance elongated in the order: 2.02 Å (CL) <2.07 Å (NL) <2.145 Å (BL) <2.28 Å (bi-PL) <2.29 Å (ter-PL) <2.305 Å (PL) <2.32 Å(Cl) <2.355 Å (tetra-PL) <2.44 Å (Br) <2.648 Å (I). The mean Pt(IV)-L bond distance elongated in the order: 1.88 Å (CO) <2.07 Å (CL) <2.14 Å (bi-CL) <2.16 Å (ter-CL) <2.175 Å (tetra-CL) <2.23 Å (ter-NL) <2.44 Å (Cl) <2.87 Å (I). The mean Sn(II)-L bond distance elongated in the order: 2.15 Å (CL) <2.31 Å (penta-BL) <2.355 Å (Cl) <2.52 Å (Br). In the example with chelating ligands, electronic and steric factors both play a role in the resultant geometry and is reflected in the L-Pt-L ring angles of the respective metallocycles. The mean L-Pt(II)-L angle opens in the order: 48.5° (CS) <84.5° (PC$_2$P) and L-Pt(IV)-L: 39.0° (CC) <66.0° (CCC) <76.4° (NC$_2$N, unsaturation) <85.0° (NC$_2$N, saturation). There are 19 examples in which exist a direct Pt(II)-Sn(II) bond, ranging from 2.486(1) Å (Nelson et al., 1996) to 2.651(1) Å (Marx and Wesermann, 2000) (average 2.582 Å). In 10 Pt(IV)-Sn(II) derivatives a bond exists, ranging from 2.493(1) Å (Janzen et al., 2001) to 2.573(1) Å (Canty et al., 1999) (average 2.544 Å). Whereas the Pt(II) atom prefers a square-planar, the Pt(IV) atom a tetragonal bipyramidal and Sn(II) atom a tetrahedral geometry.

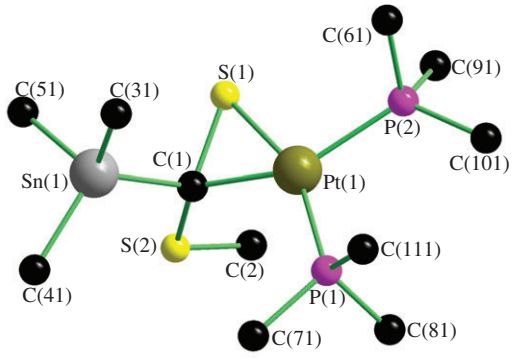

Figure 3 Structure of (PPh$_3$)$_2$Pt(Ph$_3$SnC(S)SMe) (phenyl groups are omitted for clarity) (Carr et al., 1983).

There are three PtPb dimers, in monoclinic pale yellow (Crociani et al., 1973), two units Pt(PPh$_3$)$_2$(Ph) with Pb(Ph)$_3$ are connected only by a direct Pt(II)-Pb(II) bond [2.698(10) Å]. Both metal atoms are four-coordinated, PtP$_2$CPb (square-planar) and PbC$_3$Pt(tetrahedral). In colourless monoclinic Pt(II)Pb(II) dimer (Balch and Rowley, 1990; Balch et al., 1993), Pt(CN)$_2$ and Pb(η^2-ac) units are connected by crown P$_2$ ligand which bound to Pt via two P and to Pb via four O and two N donor sites (Figure 4).

The Pt-Pb separation is 3.313(2) Å. The Pt(II) atom has a square-planar geometry (PtC$_2$P$_2$), the Pb(II) atom is eight-coordinated (PbO$_6$N$_2$). In triclinic Pt(IV)-Pb(II) dimer (Albano et al., 1995), two units Pt(η^2-Me$_2$phen)Cl and Pb(Ph)$_2$ are connected by Pt-Pb bond [2.642(1)Å] and by Me$_2$mal ligand which bound to the Pt via two C atoms and to the Pb via O atom. The Pt(IV) atom has a pseudo-octahedral (PtN$_2$C$_2$ClPb) and Pb(II) atom a trigonal-bipyramidal (PbC$_2$OClPt) environment.

PtM (M=Ga, In, Tl or Sb) complexes

A yellow monoclinic PtGa dimer (Fischer et al., 1990) is the only example of such metal centres. Two units Pt(η^2-dcpe)(η^1-npe) and Ga(η^1-npe)$_2$ are connected only via Pt-Ga bond [2.438(1) Å]. The Pt(II) atom has a square-planar (PtP$_2$CGa) and Ga atom is three-coordinated (GaC$_2$Pt). A colourless PtIn dimer (Fischer and Behm, 1991) is also the only example of such metal centres. Two units Pt(η^2-dcpe)(η^1-CH$_2$SiMe$_3$) and In(η^1-CH$_2$SiMe$_3$)$_2$ are connected only via a direct Pt-In bond [2.6012(2) Å]. The Pt atom has a

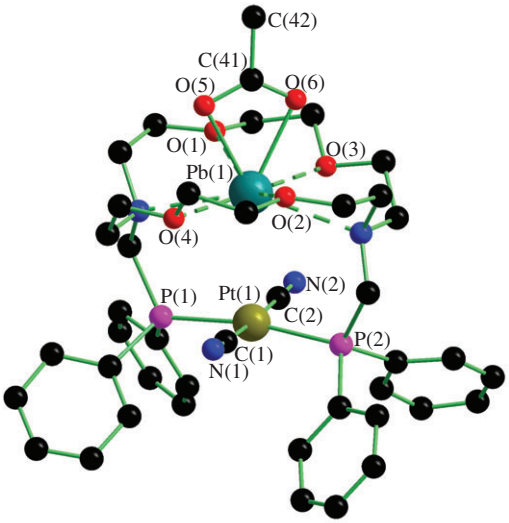

Figure 4 Structure of [Pt(CN)$_2$(μ-crownP$_2$)Pb(ac)] (Balch et al., 1993).

square-planar geometry (PtP_2ClIn) and In atom a trigonal-planar (InC_2Pt).

There are six Pt(IV)Tl(I) (two examples), Pt(0)Tl(I) (two examples), Pt(II)Tl(I) (two examples) dimers, for which structural parameters are available. In monoclinic Pt(IV)Tl(I) dimers (Ma et al., 2002), two units $Pt(CN)_5$ with $Tl(dmso)_3(\eta^2\text{-phen})$, and $Pt(CN)_5$ with $Tl(\eta^2\text{-phen})_2$ are connected only via direct Pt-Tl bonds [2.6296(3) and 2.6375(5) Å], respectively. Each metal centre is six-coordinated, PtC_5Tl and TlO_3N_2Pt. In triclinic Pt(0)Tl(I) dimers (Balch and Rowley, 1990; Balch et al., 1993; Catalano et al., 2001), $Pt(PPh_3)_3$ (Balch and Rowley, 1990; Balch et al., 1993) and $Pt(PPh_2py)_3$ (Catalano et al., 2001) are bound via Pt atom to Tl(I) atom, with Pt(0)-Tl(I) bond distances of 2.888(5) Å (Balch and Rowley, 1990; Balch et al., 1993) and 2.8653(9) Å (Catalano et al., 2001). Whereas the Pt(0) are four-coordinated (PtP_3Tl), the Tl(I) are linear (TlPt). In Pt(II)Tl(I), monoclinic (Balch and Rowley, 1990; Balch et al., 1993), which contains two crystallographically independent dimers, $Pt(CN)_2$ units are connected to Tl(I) by a bridging crown P_2 ligand via two P atoms to Pt(II) and four O and two N atoms to Tl(I) atom (PtC_2P_2, TlO_4N_2). The Pt-Tl bond distances are 2.911(2) and 2.958(2) Å. In triclinic Pt(II)Tl(I) dimer (Figure 5) (Uson et al., 1997) $Pt(C_6F_5)_2(PPh_3)$ unit is connected to Tl atom, by a direct Pt-Tl bond [2.994(1) Å] and in addition acetate group via O carboxylate O atoms (anti-anti fashion) bridging the metal centres (PtC_2OPTl and TlOPt). The mean Pt-Tl(I) bond distance elongated in the sequence: 2.633 Å (Pt(IV)) <2.876 Å (Pt(O)) <2.952 (Pt(II)).

There are six PtSb dimers, in five of them two units of respective metal centres, namely, $PtBr_2(PPh_3)$ with $Sb(Ph)_3$ (triclinic), and $PtBr_3$ with $Sb(Ph)_3$ (monoclinic) (Gomez and Hernandez, 2000); $Pt(\eta^4\text{-}C_4Me_4)Cl_2$ with $Sb(Ph)_3$ (Heinemann et al., 1996), $Pt(PEt_3)_2Cl$ with $Sb(\eta^1\text{-}C_{10}H_{10}O)_2$ (Jones et al., 2001) and $Pt(PPh_3)_2Me$ with $Sb(\eta^3\text{-ad})$ (Stewart and Arduengo, 1986) are connected via a direct Pt-Sb bond with length which elongated in the sequence: 2.463(2) Å (tr) (Gomez and Hernandez, 2000) <2.496(2) Å (m) (Gomez and Hernandez, 2000) <2.5911(4) Å (Heinemann et al., 1996) <2.6042(4) (Jones et al., 2001) <2.641(1) Å (Stewart and Arduengo, 1986). The metal centres have the following chromophores: $PtBr_2PSb$ and SbC_3Pt (triclinic) (Gomez and Hernandez, 2000), $PtBr_3Sb$ and SbC_3Pt (monoclinic) (Gomez and Hernandez, 2000), PtC_4Cl_2Sb and SbC_3Pt (Heinemann et al., 1996), PtP_2ClSb and SbC_2Pt (Jones et al., 2001) and PtP_2CSb and SbO_2NPt (Stewart and Arduengo, 1986). In yellow orthorhombic PtSb (Black et al., 1997), $Pt(PEt_3)_2Cl$ moiety is connected with Sb atom via P atom to Pt and via another P and C of $P_2C_2Bu^t_2$ ligand (PtP_3Cl and SbCP).

PtM (M=Zn, Cd or Hg) complexes

There are 25 PtM [M=Zn (×5), Cd (×4), Hg (×18)] dimers for which structural parameters are available. In monoclinic yellow Pt(II)Zn(II) dimer (Figure 6) (Schöhorn et al., 1985), two units $Pt(NH_3)_2$ and $Zn(H_2O)_3$ are bridged by two heterobidentate 1-methyluracilate ligands via N to Pt(II) and via O to Zn(II). The Pt-Zn bond distance is 2.760(1) Å. The Pt(II) has a trigonal bipyramidal (PtN_4Zn) arrangement, the Zn(II) a pseudo-octahedral (ZnO_5Pt).

In another yellow orthorhombic Pt(II)Zn(II) dimer (Crociani et al., 1994), two moieties $Pt(\eta^2\text{-dppe})$ and $ZnCl_2$ are connected by heterobidentate-C,N C_5H_4N and C(OEt) NHC_6H_4OMe-E ligands. Both of the bridged ligands are coordinated to the Pt(II) via C atom (PtC_2P_2) and to Zn(II) via N (ZnN_2Cl_2). The Pt-Zn separation of 3.238(1) Å ruled

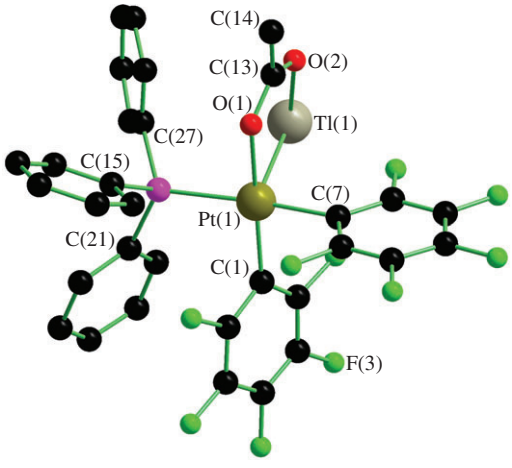

Figure 5 Structure of $[Pt(C_6F_5)_2(PPh_3)(\mu\text{-ac})Tl]$ (Uson et al., 1997).

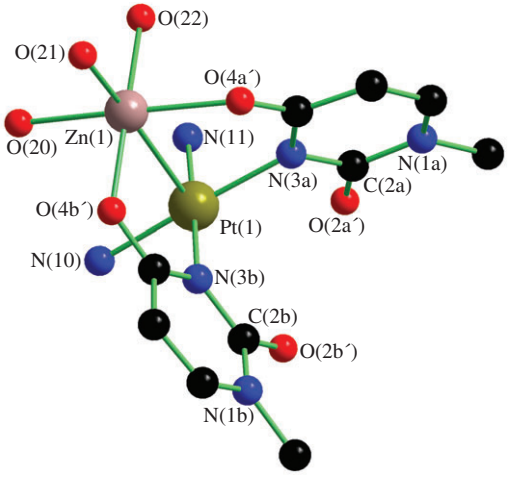

Figure 6 Structure of $[Pt(NH_3)_2(\mu\text{-Meura})_2Zn(H_2O)_3]$ (Schöhorn et al., 1985).

out bond. Another three-heterobidentate-S,O ligands [S(O)$P(OPr^i)_2]_3$ bridged Pt(PMe_2Ph) unit and ZnCl, via S to Pt(II) and via O to Zn(II) (Phillips et al., 1995). Both metal centres are four-coordinated, PtS_3P, square-planar and ZnO_3Cl a tetrahedral. The Pt-Zn separation is 4.39 Å. In yellow monoclinic Pt(II)Zn(II) dimer (Poat et al., 1990), two $S(O)P(OPr^i)_2$ serve as bridges between $Pt(PMe_2Ph)_2$ and $ZnCl_2$ in a similar manner as in Phillips et al. (1995) and completed four-coordination about each metal centres (PtS_2P_2, square-planar, ZnO_2Cl_2, tetrahedral). In this dimer, the Pt-Zn separation is also 4.39 Å. In another yellow monoclinic Pt(II)Zn(II) dimer (Sembiting et al., 1999), the Pt atom is connected with $ZnBr_2$ unit by two heterobidentate-O,P Ph_2PthqH ligands. The O atom of each ligand serve as bridges ($Pt(O)_2Zn$) and, in addition, P atom of each ligand coordinated to the Pt(II) atom. Both metal centres are four-coordinated, PtO_2P_2 (square-planar) and ZnO_2Br_2 (tetrahedral).

In two monoclinic yellow Pt(II)Cd(II) dimers (Figure 7) (Yamaguchi et al., 1999), two units Pt(η^2-bpy)$(Me)_2$ or Pt(η^2-phpy) with Cd(η^4-cyclen) are connected only via Pt-Cd bonds, 2.6101(8) and 2.6389(9) Å. Each M(II) atom is five-coordinated (PtN_2C_2Cd and CdN_4Pt).

As was already mentioned, Hg as a partner with Pt occurs more often than Zn or Cd. In yellow orthorhombic Pt(II)Hg(II) dimer (van der Ploeg et al., 1980, 1982a), two units Pt(η^2-danp)$_2$ and Hg(η^1-ac) are connected by a direct Pt-Hg bond [2.513(1) Å] as well as acetate ligand which serve as a bridge via O atoms of the carboxylate group. The Pt(II) is hexa-coordinated (PtN_2C_2PHg) and Hg(II) three- (HgO_2Pt) of T shape. In another seven PtHg dimers (Kuzmina et al., 1978; Bashilov et al., 1988; Ghilardi et al., 1989; Cucciolito et al., 1993; Batten et al., 1997; Forniés et al., 2000; Schuh et al., 2001), only a direct Pt-Hg bond connecting the following units: Pt[η^4-$N(CH_2CH_2PPh_2)_3$] with HgMe (Ghilardi et al., 1989); Pt(η^4-pp_3) with HgCl (Schuh et al., 2001), Pt(η^2-mpt)(η^2-Me_2NCS_2)(η^1-F_3ac) with Hg(η^1-F_3ac) (Forniés et al., 2000); Pt(η^2-Me_2phen)(η^2-$MeO_2CCH{=}CHCO_2Me$)Cl with HgMe (Cucciolito et al., 1993); Pt$(PPh_3)_2$Cl with Hg(η^1-camph-1-enyl) (Bashilov et al., 1988), Pt$(PPh_3)_2(CF_3)$ with Hg(CF_3) (Kuzmina et al., 1978) and Pt(η^5-$CB_{10}H_{11}$)$(PEt_3)_2$ with HgPh (Batten et al., 1997). The Pt-Hg bond elongated in the same order: 2.531(1) Å (Ghilardi et al., 1989) <2.5511(9) Å (Schuh et al., 2001) <2.5537(7) Å (Forniés et al., 2000) <2.558(1) Å (Cucciolito et al., 1993) <2.561(2) Å (Bashilov et al., 1988) <2.569(2) Å (Kuzmina et al., 1978) <2.5850(5) Å (Batten et al., 1997). Each Hg(II) atom is almost linearly coordinated HgXPt [X=C (Kuzmina et al., 1978; Bashilov et al., 1988; Ghilardi et al., 1989; Cucciolito et al., 1993; Batten et al., 1997; Forniés et al., 2000) or Cl (Schuh et al., 2001)] with the mean X-Hg-Pt angle of 173.5°. The Pt atoms have the chromophores: PtP_3NHg (Ghilardi et al., 1989), PtP_4Hg (Schuh et al., 2001), PtS_2OCPHg (Forniés et al., 2000), PtN_4ClHg (Cucciolito et al., 1993), PtP_2XHg [X=Cl (Bashilov et al., 1988), C (Kuzmina et al., 1978)] and PtB_4CP_2Hg (Batten et al., 1997). There four yellow monoclinic Pt(II)Hg(II) dimers (Krumm et al., 1993; Müller et al., 1998) in which Pt$(NH_3)_2$ or Pt$(NH_2Me)_2$ are connected with Hg(II) atom via two homobidentate-N,N′ non-chelating methylcytosinate or dimethylcytosinate. The Pt-Hg bond length elongated in the order: 2.7496(6) Å (Müller et al., 1998) <2.765(2) Å (Krumm et al., 1993) <2.765(1) Å (Krumm et al., 1993) <2.835(1) Å (Krumm et al., 1993). Each Pt(II) atom is five-coordinated (PtN_4Hg) and Hg(II) is three-coordinated (HgN_2Pt, T shape).

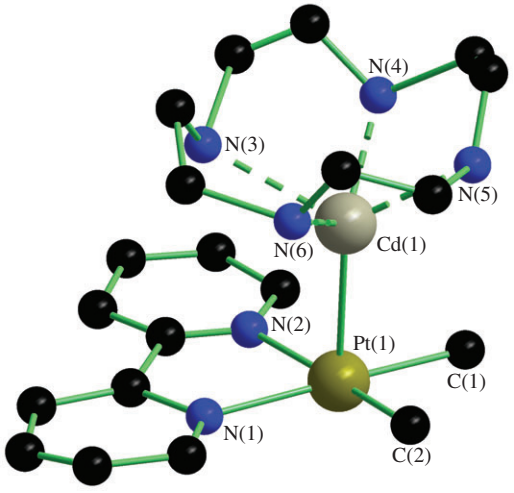

Figure 7 Structure of [Pt(bpy)$(Me)_2$Cd(cyclen)] (Yamaguchi et al., 1999).

In monoclinic orange Pt(II)Hg(II) dimer (van der Ploeg et al., 1982b,c) Pt(η^3-damp) with HgClBr are bridged by non-chelating bidentate-N,N′ tcap ligand. The Pt-Hg distance is 2.8331(7) Å. The Pt(II) atom is five-PtN_3CHg and Ht(II) atom four-HgNClBrPt coordinated. In orthorhombic yellow Pt(II)Hg(II) dimer (Bennett et al., 2002), $PtCl_2$ and $HgCl_2$ units are connected by a pair of heterobidentate $Ph_2PC_6H_4$ ligands via P atom to Pt(II) and via C atoms to Hg(II) atom. The Pt-Hg distance is 2.8339(7) Å. The inner coordination spheres about the metal centres are $PtCl_2P_2Hg$ and HgC_2Pt (T shape). In monoclinic white dimer (Bennett et al., 2002), two units Pt(η^2-$Ph_2PC_6H_4$) and HgCl are connected by a pair of $Ph_2PC_6H_4$ ligands in a similar manner than in the orthorhombic complex (Bennett et al., 2002), but Pt-Hg separation is much longer: 3.1335(5) Å. In another orthorhombic white dimer (Xu et al., 1996), a pair of homobidentate (P,P″) non-chelating dppm ligands serve as bridges between Pt(Me)Cl and $HgCl_2$. The Pt-Hg separation is 3.302(1) Å. Both metal centres are

four-coordinated, PtP_2CCl (square-planar) and $HgCl_2P_2$ (tetrahedral). In monoclinic white Pt(II)Hg(II) dimer (Figure 8) (Berenguéz et al., 1994), a pair of C≡CSiMe$_3$ ligands serve as bridges via their C atoms, between $Pt(C_6F_5)_2$ and $HgBr_2$ units. The mean Pt-C-Hg bond angles is 104.2(9)° and Pt-Hg separation is 3.627(5) Å. The Pt(II) atom has a square-planar (PtC_4) and Hg(II) a pseudo-octahedral (HgC_4Br_2) arrangement.

In another monoclinic white dimer (Baker et al., 1972), a pair of Cl atoms serve as bridges between $Pt(PMe_2Ph)_2$ and $HgCl_2$ units [Pt-Hg=4.037(2) Å]. Each metal centre is four-coordinated ($PtCl_2P_2$ and $HgCl_4$).

The mean Pt-L bond distance in this series elongated in the order: 2.05 Å (NL) <2.06 Å (bi-CL) <2.10 Å (CL) <2.15 Å (bi-NL) <2.16 Å (OL) <2.275 Å (tetra-PL) <2.30 Å (bi-PL) <2.31 Å (PL) <2.40 Å (bi-SL) <2.42 Å (Cl). The mean Zn-L bond distance elongated in the order: 2.08 Å (OL) <2.225 Å (Cl) <2.345 Å (Br). The mean Cd-N (tetra) bond distance is 2.35 Å and the mean Hg-L elongated in the order: 2.095 Å (CL) <2.12 Å (OL) <2.485 Å (Cl) <2.545 Å (Br). There are homo- as well as hetero-bidentate ligands which serve as bridges between the Pt-Hg and the mean values: (Pt-L vs. Hg-L): 2.15 vs. 2.62 Å (O + O); 2.06 vs. 2.095 Å (N + N); 1.965 vs. 2.5 Å (C + C); 2.278 vs. 2.497 Å (P + P); 2.318 vs. 2.24 Å (P + C), 2.37 vs. 2.84 Å (μCl). The mean Pt-L vs. Zn-L bond distances are: 2.045 vs. 2.065 Å (N + O), 2.04 vs. 2.04 Å (C + N), 2.145 vs. 2.015 Å (P + O) and 2.375 vs. 1.915 Å (S + O). In the examples with chelating ligands, electronic and steric factors both play a role in the resultant geometry and is reflected in the L-Pt-L ring angles of the respective metallocycles. The mean L-Pt-L angle opens in the sequence: 41.4° (CC) <43.3° (CB) <48.3° (BB) <73.6° (SS) <76.3° (NC$_2$N) <80.5° (NC$_2$C) <82.8° (PC$_2$P).

PtM (M=Na, K or Ca) complexes

A triclinic colourless Pt(II)Na(I) dimer (Figure 9) (Freisinger et al., 2000) is the only example of such metal centres. In this dimer, a pair of mquaH ligands with one mcyt ligand serve as bridges, each of the ligands via one N atom to Pt(II) and via O atom to Na(I) between $Pt(NH_3)$ and $Na(H_2O)_2(OClO_3)$ units. The Pt(II) has a square-planar (PtN_4) and Na(I) has a pseudo-octahedral (NaO_6) environment. In monoclinic colourless Pt(II)K(I) dimer (Freisinger et al., 2000), a pair of mcyt ligand connected $Pt(NH_3)_2$ and $K(F_2PF_4)_2$ units in a similar manner as in Pt(II)Na(I) dimer. The Pt(II) has a square-planar (PtN_4) and K(I) a compressed tetragonal bipyramidal (KF_4O_2) arrangement with O atoms at axial positions. In Pt(II)Ca(II) dimer (Figure 10) (Davidson et al., 1991), a pair of heterobidentate-S,N mbo ligands serve as bridges between Pt(II) and CaCl units. Each of the ligands bound Pt(II) via S and Ca(II) via N atom (PtS_4 and CaN_4Cl). The Pt-Ca distance is 2.950(5) Å.

Conclusions

There are 90 PtM dimers for which structural parameters were analysed. These complexes crystallised in the following crystal classes: monoclinic (55.5%) > triclinic (27%) > orthorhombic (16.5%) > tetragonal (1%). A yellow coloured complex by far most prevailed (55.5%) followed with colourless (29%) and some orange/red (3.5%) and white (2%).

These complexes can be divided into three groups: the first in which only a direct Pt-M bond connects the respective units (59%), the second in which a direct Pt-M

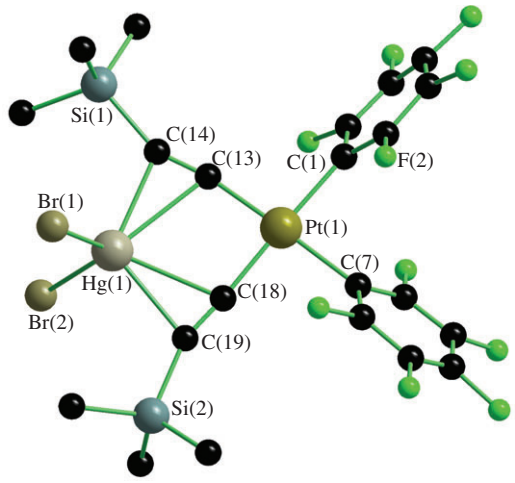

Figure 8 Structure of [Pt $(C_6F_5)_2(\mu\text{-}C{\equiv}CSiMe_3)_2HgBr_2$] (Berenguéz et al., 1994).

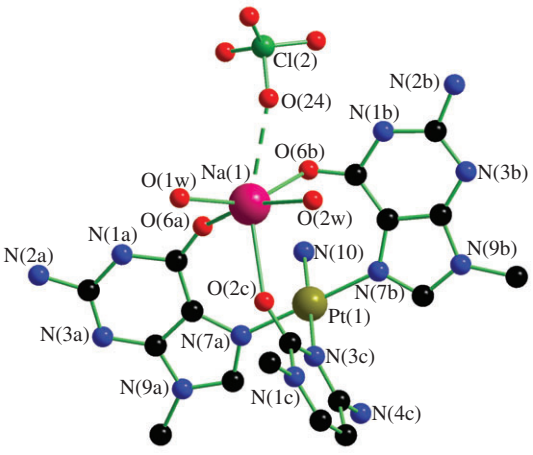

Figure 9 Structure of [Pt$(NH_3)(\mu\text{-mquaH})_2(\mu\text{-mcyt})Na(H_2O)_3(OClO_3)$] (Freisinger et al., 2000).

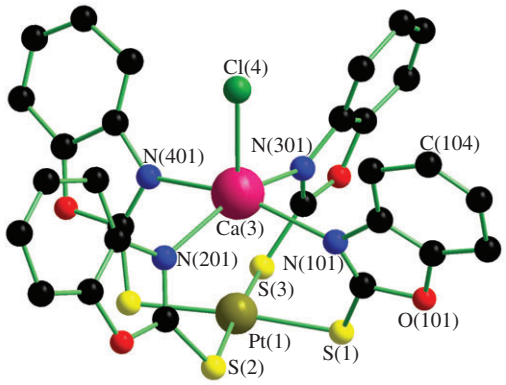

Figure 10 Structure of [Pt (μ-mbo)$_4$CaCl] (Davidson et al., 1991).

bond and bridge/s ligand/s are present (33%), and the third one in which only bridge/s ligand/s serve as bridge/bridges between the respective units (8%). The Pt atoms are found in oxidation states 0, +2 (most common) and +4. The Pt(0) is three-coordinated; Pt(II) four- (by far prevails) and five-, Pt(IV) five-, six- (most common), seven- and even eight-coordinated. Four-coordinate Pt(II) atoms are with varying degrees of distortion from square-planar. The ligands range from unidentate, through bi-, tri-, tetra-, penta- and octadentate. The most common donor atoms are P, C, Cl and N. The mean Pt-P bond distance elongates with the size of the P-donor ligand in the order: 2.265 Å (PEt_3) <2.275 Å ($PPhMe_2$) <2.288 Å (PPh_3). All of them elongates as a result of the trans influence (of Ge, Sn or C) in the order: 2.330 Å ($PPhMe_2$) <2.340 Å (PPh_3) <2.346 Å (PEt_3). The mean Pt-L bond distances follow this trend: L=Cl (2.337 vs. 2.458 Å); L=Br (2.417 vs. 2.509 Å). The mean Pt-C bond distance elongates in the order: 1.88 Å (CO) <2.00 Å (CN or CNR) <2.055 Å (Ph) <2.06 Å (Me). The mean Pt-L (unidentate) value increases in the order: 2.04 Å (CL) <2.15 Å (NL) <2.305 Å (PL) <2.405 Å (Cl) <2.472 Å (Br) <2.785 Å (I). This reflects the radii of the corresponding atom except in the cases of N-donors or the Cl atom. For homobidentate ligands the order is: 2.12 Å (CL) <2.13 Å (NL) <2.28 Å (PL) <2.40 Å (SL).

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

In the examples with chelating ligands, electronic and steric factors both play a role in the resultant geometry and is reflected in the L-Pt-L bite angle opens in the order: 39.5° (CC) <43.3° (CB) <48.3° (BB) <48.5° (CS) <68° (CCP) <73.6° (SCS) <75.7° (NC_2N, unsaturation) <80.5° (NC_2N, saturation) <86.5° (PC_2P). Some complexes containing Pt-Ge bonds generate 4-, 5- and 6-membered rings with values: 64.7° (PtCOGe) <66.0° (PtNCGe) <76.5° ($PtNC_2Ge$) <82.3° (PtSNOGe) and 77.0° (PtOCNOGe). The mean Pt-M bond distance elongated in the order: 2.425 Å (M=Ge) <2.438 Å (Ga) <2.559 Å (Sb) <2.601 Å (In) <2.625 Å (Cd) <2.657 Å (Hg) <2.660 Å (Sn) <2.670 Å (Pb) <2.674 Å (Tl) <2.760 Å (Zn) <2.960 Å (Ca).

There are four dimers, PtSn (Farkas et al., 1996; Levy et al., 1996b; Dahlenburg and Martel, 2001) and PtTl (Balch and Rowley, 1990; Balch et al., 1993) which contain two crystallographically independent molecules differing mostly by degree of distortion of the M-M, M-L distances and L-M-L angles. These represent examples of distortion isomerism (Melník 1982; Melník and Holloway, 2006). Structural characterisation of heterotrimeric complexes are in progress.

Acknowledgements: The authors are grateful to Michael Lutter and Klaus Jurkschat from Technical University Dortmund, Germany for technical assistance.

Received July 19, 2012; accepted October 4, 2012; previously published online November 23, 2012

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