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Review

The chemistry of tri- and high-nuclearity palladium(II) and platinum(II) complexes

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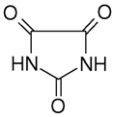
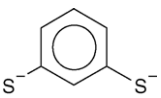
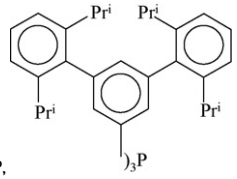
Contents

Abbreviations: 4-Mepy, 4-methylpyridine; acac, $CH_3C(O)CHC(O)CH_3$; aet, 2-aminoethanethiolate ($H_2NCH_2CH_2S^-$); bipy, 2,2′-bipyridine; Bz, benzyl (–CH_2Ph); COD, 1,5-cyclooctadiene; dmap, 4-Me_2N–C_5H_4N; dmf, dimethylformamide; dmpH, 2-(dimethylaminoethyl)phenyl; dmpm, $Me_2PCH_2PMe_2$; dmpzH, 3,5-dimethylpyrazole; dmso, dimethylsulfoxide; dpae, 1,2-bis(diphenylarsino)ethane; dpm, $Bu^t(CO)CHCOBu^t$; dpmp, $Ph_2PCH_2P(Ph)CH_2PPh_2$; dppb, $Ph_2P(CH_2)_4PPh_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; dppf, bis(diphenylphosphino)ferrocene; dppfc, diphenylphosphino ferrocene; dppm, $Ph_2PCH_2PPh_2$; dppp, $Ph_2P(CH_2)_3PPh_2$; dtc, $Et_2NCS_2^-$; en, ethylenediamine; H_2bim, 2,2′-bis-imidazole; hfac, $CF_3C(O)CHC(O)CF_3$; Hpymo, 2-hydroxypyrimidine; Me_2bipy, 4,4′-dimehtyl-2,2′-bipyridine; Me_2phen, 4,7-dimethyl-1,10-phenanthroline; OTf, $CF_3SO_3^-$;



parabanic acid, ; phen, 1,10-phenanthroline; pic, (2-NC_5H_4)COO or picolinate; pop, $P_2O_5H_2^{2-}$; pyS_2,  ; pySH, 2-mercaptopyridine; pzH, pyrazole; SC_4H_8 or tht, tetrahydrothiophene; $SpmMe_2$, pyrimidene-4,6-dimethyl-2-thionate; Tbt, 2,4,6-tris{bis(trimethylsilyl)methyl}phenyl; terpy, 2,2′:6′,2″-terpyridine;



Th, 2-thienyl; thf, tetrahydrofuran; tmeda, $Me_2NCH_2CH_2NMe_2$; TRIP, ; ttzh, 1,3-thiazolidine-2-thione; xyl, 2,6-$Me_2C_6H_3$.

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ABSTRACT

This review gives an overview of the progress on tri- and high-nuclearity palladium(II) platinum(II) complexes and discusses recent developments in the chemistry of these complexes. Three or more square-planar metal atoms can be assembled in several ways resulting into myriad geometric forms of the resulting complexes. These square planes may be sharing a corner, an edge and two edges or even separated by ligands having their donor atoms incapable of forming chelates yielding dendrimers and self-assembled molecules. A variety of ligands have been used to stabilize these complexes. The chemistry of these complexes has been dealt based on nuclearity of the complexes. Synthetic, spectroscopic, structural aspects and applications of these complexes are described in this review.

1. Introduction

Recently we reviewed the chemistry of binuclear palladium(II) and platinum(II) complexes [1]. The metal square planes in these complexes are held together in several ways with predominance of complexes formed by ligands sharing two edges of the square (Scheme 1). Subtle changes in the nature of ligating atom, ligand bite or auxiliary ligands lead to different stereochemistry, conformation of the molecule and diverse reactivity.

As one moves from binuclear derivatives to high-nuclearity palladium(II) and platinum(II) complexes, the metal square planes can be arranged in several ways and the number of possible arrangements increases with increasing number of participating metal atoms. The metal square planes may be assembled either by sharing ligands between metal coordination sphere or in a dendritic fashion. Both classes of complexes show a great diversity in terms of structural feature and chemical reactivity.

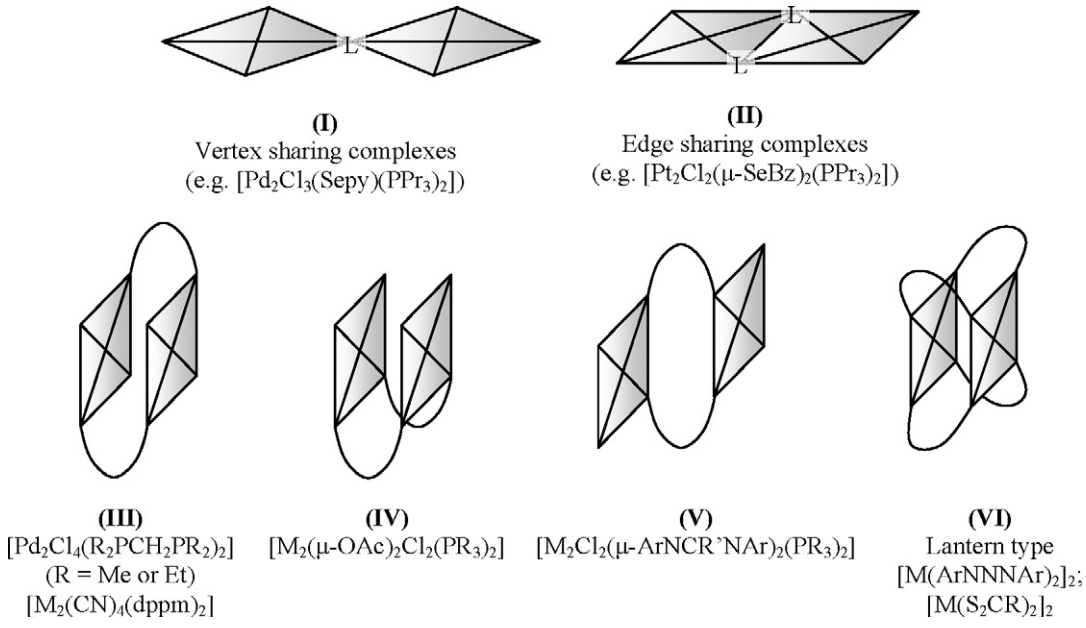
Unlike binuclear complexes, which have been synthesized and studied over the past several decades, the tri- and high-nuclearity complexes have attracted considerable attention during the past 15 years or so, although insoluble polynuclear thiolato derivatives have been described in older literature [2–4]. These complexes have been isolated either by default or through design. The progress in tri- and high-nuclearity complexes has been facilitated by our understanding in not only developing convenient synthetic strategies and but also by the advances in instrumentation (*e.g.*, X-ray crystallography) which has helped in characterization of such complexes.

Tri- and high-nuclearity complexes formed by weak non-covalent interactions such as $d^8\cdots d^8$ (M···M, *e.g.*, $[Pt(S_2CR)_2]$ [5], $[Pt(CN)_4]^{2-}$ [6,7]), π···π (*e.g.*, $[\{Pt(Me_2bipy)_2\}\{PtCl_2(Me_2bipy)\}_2][PF_6]_2$ [8]) and C–H–O are beyond the scope of this review. One-dimensional self-stacked chain complexes, like Magnus' green salt ($[Pt(NH_3)_4][PtCl_4]$) [9], mixed valent oligomeric "platinum blue" [10–13] and halogen bridged MMX chain compounds (*e.g.*, $[Pt_2(pop)_4X]^{4-}\cdot nH_2O$ and $[M_2(S_2CR)_4I]_\infty$ (M = Pd or Pt) [14–16] are also excluded. Mixed metal complexes, in spite of having desired Pd or Pt nuclearity (*e.g.*, "Pd_3W") are also excluded.

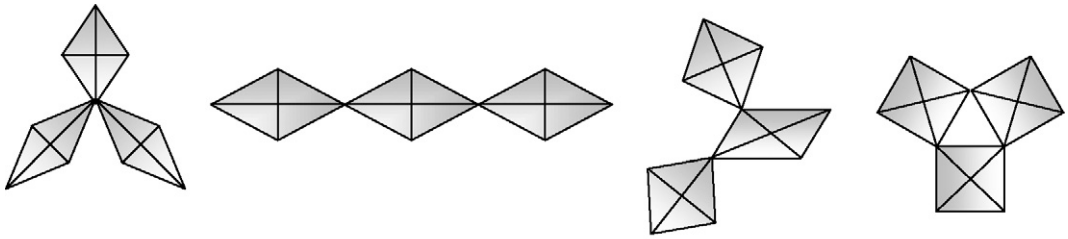
2. Trinuclear complexes

2.1. Corner sharing trinuclear complexes

Four different structural motifs of corner sharing (**VII**–**X**, Scheme 2) trinuclear palladium and platinum complexes have been identified. The structural motif where three metal square planes sharing a corner (**VII**) has been reported from the author's group for allylpalladium complexes, $[Pd_3Cl_2(SeCH_2CH_2NMe_2)(\eta\text{-allyl})_3]$ (allyl = C_3H_5 or C_4H_7) [17]. These complexes are readily obtained by



Scheme 1.



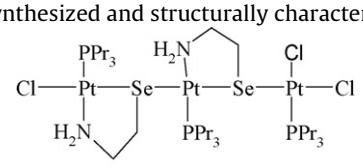
Scheme 2.

the reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with $[Pb(SeCH_2CH_2NMe_2)_2]$ in benzene. One of the palladium atoms is bound with the chelated selenolate ligand while the other two-palladium atoms are each coordinated with selenium atom, an allyl group and the chloride ion (Fig. 1). The selenolate ligand acts in a triply bridging fashion. A dicationic complex containing triply bridging hydroxo group, $[Pt_3(\mu_3\text{-}OH)(OPPh_2)_3(PR_3)_3]^{2+}$ (PR_3 = $PMePh_2$, PPh_3), has been prepared by the reaction of $[Pt_2(\mu\text{-}OH)_2(OPPh_2)_2(PR_3)_2]$ with HBF_4 or HPF_6 [18].

Trinuclear palladium and platinum complexes in which central metal square plane sharing corners with terminal metal atoms, either in *trans* (**VIII**) or *cis* (**IX**) configuration, have been synthesized and characterized. Reaction of $PtCl_2(COD)$ with *cis*-$[PtCl_2(dpmp)]$ gives a mixture of *cis*- and *trans*-$[PtCl_2\{cis\text{-}PtCl_2(dpmp)\}_2]$. The two isomers could be separated by fractional crystallization. The *trans* isomer has been structurally characterized [19]. Treatment of *trans*-$[Pd(CN)_2(PPh_3)_2]$ with two equivalents of $[Pd(C_6F_5)(ClO_4)(PPh_3)_2]$ in benzene gives a cyano-bridged trinuclear complex *trans*-$[\{Pd(C_6F_5)(PPh_3)_2\}_2(\mu\text{-}CN)_2Pd(PPh_3)_2][ClO_4]_2$ in 82% yield [20].

The sulfur atom in homoleptic dithiocarbamate complexes can be employed for ligation. Such a behavior has been reported for some dithiocarbamate complexes of palladium. Thus the reaction of $[Nb_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]$ with $PdCl_2(PhCN)_2$ in dichloromethane afforded an orange crystalline product, $[Pd_3Cl_2(dtc)_4]\cdot 2CH_2Cl_2$ in 73% yield [21]. Recrystallization of a palladium(IV) dithiocarbamate complex, $[PdBr_2(dtc)_2]$, from chloroform–cyclohexane results into the formation of a trinuclear palladium(II) complex, $[Pd_3Br_2(dtc)_4]$ as a by product in very poor yield [22]. Both the chloro- and bromo-complexes have been structurally characterized (Table 1). One of the sulfur atoms from each dtc ligand of central palladium atom are coordinated to the terminal "PdX(dtc)" fragments which are mutually *trans* (one above and other below the planar central PdS_4 core) (Fig. 2) [21,22].

A linear *trans*-configured (type-**VIII**) trinuclear homo- and hetero-metallic chalcogenolate complexes have been synthesized using the reaction route shown in Scheme 3. The mass spectra exhibit peaks either due to molecular ion or [M–Cl] with expected isotopic pattern. The ^1J(Pt–P) coupling constants are reduced by 45–80 Hz with respect to the one observed for mononuclear complexes [23]. The X-ray structural analysis of $[\{PtCl(SeCH_2CH_2NMe_2)(PEt_3)\}_2PtCl_2]$ (Fig. 3) reveals that the central platinum atom is coordinated to mutually *trans* two Cl and two selenium atoms, while the terminal platinum atoms are surrounded by chelating $SeCH_2CH_2NMe_2$ group and a chloride and PEt_3 ligand with P and N atoms in a *trans* position [23]. A complex in which the coordination environment around each platinum atom defined by different ligating atoms, $[PtCl(PPr_3)(NH_2CH_2CH_2Se)Pt(PPr_3)(NH_2CH_2CH_2Se)PtCl_2(PPr_3)]$ (**1**) has been synthesized and structurally characterised [24].



(1)

Neutral sulfur ligands, such as disulfides and thioethers, have been employed to prepare trinuclear platinum complexes [25,26]. The reactions of MCl_2 with dibenzyldisulfide in dichloromethane give dibenzyldisulfide-bridged trinuclear complexes, $[M_3Cl_6(Bz_2S_2)_4]$ (M = Pd or Pt) [25]. These complexes have been characterized by NMR and FAB mass spectroscopy. Treatment of $[Bu_4N][Pt(C_6F_5)_3(acetone)]$ with *trans*-$[PtX_2(SC_4H_8)_2]$ (X = Cl, Br, I) in 2:1 ratio in acetone yields trinuclear platinum complexes (Eq. (1)) [26]. The central platinum atom in $[Bu_4N][PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ is coordinated to two *trans* chloride and two bridging SC_4H_8 ligands and lies on a crys-

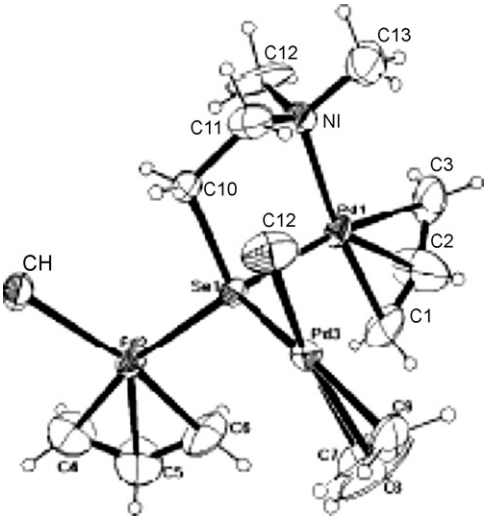


Fig. 1. Molecular structure of $[Pd_3Cl_2(SeCH_2CH_2NMe_2)(\eta\text{-}C_3H_5)_3]$; [17] (Reproduced with permission of American Chemical Society).

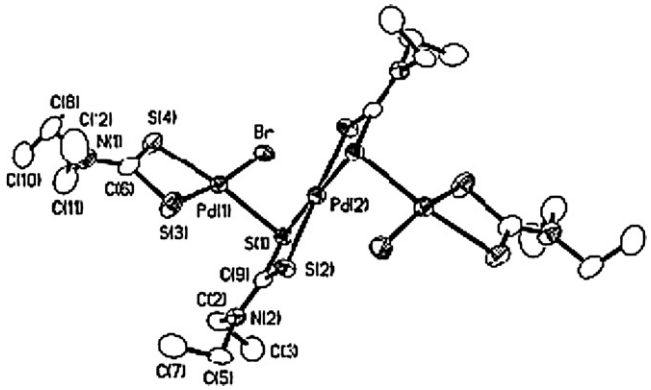
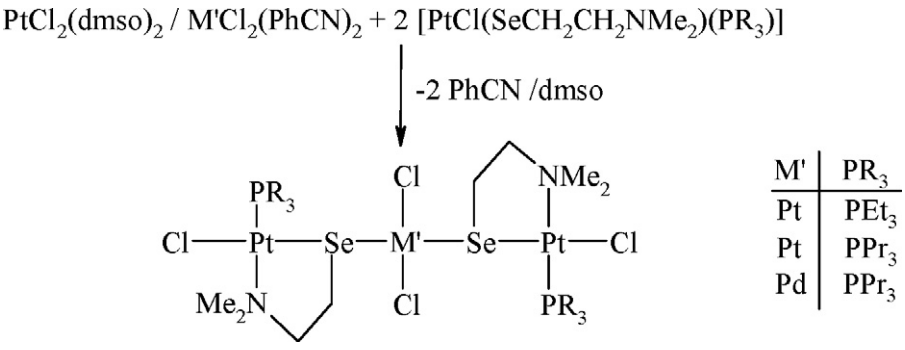


Fig. 2. Structure of $[\{(Et_2NCS_2)BrPd\}_2Pd(S_2CNEt_2)_2]$; [22] (Reproduced with the permission of Elsevier Ltd.).

Table 1
Trinuclear corner sharing palladium(II) and platinum(II) complexes characterized by X-ray crystallography.

Complex	Comment	Reference
$[Pd_3Cl_2(SeCH_2CH_2NMe_2)(\eta^3\text{-}C_3H_5)_3]$	Triply bridging selenolate Pd–Se = 2.4255–2.4968 Å	[17]
$[Pt_3(\mu\text{-}OH)(OPPh_2)_3(PMePh_2)_3][BF_4]_2$	Triply bridging OH, Pt···Pt = 3.52–3.71 Å	[18]
trans-$[PtCl_2\{cis\text{-}PtCl_2(Ph_2PCH_2P(Ph)\,CH_2PPh_2)\}_2]$	"PtP_3C_2" chelate ring adopts a distorted boat conformation; Pt–Cl = 2.271–2.372 Å	[19]
$[\{PdCl(dtc)\}_2Pd(dtc)_2]$	Pd–S = 2.2798–2.3467 Å Pd–Cl = 2.3275 Å	[21]
$[\{PdBr(dtc)\}_2(Pd(dtc)_2]$	Pd–S = 2.2827–2.3277 Å Pd–Br = 2.4602 (av) Å	[22]
$[\{PtCl(SeCH_2CH_2NMe_2)(PEt_3)\}_2PtCl_2]$	Pt–Se = 2.43 (av) Å; Chelate rings "$SeCH_2CH_2NMe_2$" adopt an *anti* configuration	[23]
$[PtCl(PPr_3)(NH_2CH_2CH_2Se)Pt(PPr_3)$ $(NH_2CH_2CH_2Se)PtCl_2(PPr_3)]$	Pt–Se = 2.4059 (15)–2.4631 (16) Å Pt–N = 2.096 (10)–2.128 (12) Å	[24]
$[PtCl_2\{(SC_4H_8)Pt(C_6F_5)_3\}_2]^{2-}$	Pt–S = 2.298 (av) Å Pt–Cl = 2.290 (av) Å	[26]
$[\{Pt(C_6F_5)_2(C{\equiv}CPh)_2\}\{PtH(PEt_3)_2\}_2]$	Pt–C = 1.984 (8)–2.443 (10) Å	[27]
$[Pt(aet)_2\{Pt(terpy)\}_2][BF_4]_4$	Pt–S = 2.295, 2.263 Å	[28]
$[Pd(aet)_2\{Pd(terpy)\}_2][PF_6]_4.2MeCN$	Pd–S = 2.256 (2)–2.299 (2) Å monomeric structure	[29]
$[Pd(aet)_2\{Pd(terpy)\}_2][BF_4]_4\cdot\frac{1}{2}H_2O$	Pd–S = 2.259 (1)–2.298 (1) Å monomeric structure	[29]
$[Pd(aet)_2\{Pd(terpy)\}_2][BF_4]_4$	Pd–S = 2.290 (1)–2.295 (1) Å polymeric structure with stacking	[29]
$[Pd(aet)_2\{Pd(terpy)\}_2][SiF_6]_2\cdot 6H_2O$	Pd–S = 2.252 (1)–2.265 (1) Å linear chain structure with alternating coplanar stacking	[29]
$[\{dppe)Pd(CS_3)\}_2Pt(C_6F_5)_2]$	Pt–S = 2.338 (S) Å Pd–S = 2.342 (4), 2.357 (4) Å	[31]



Scheme 3.

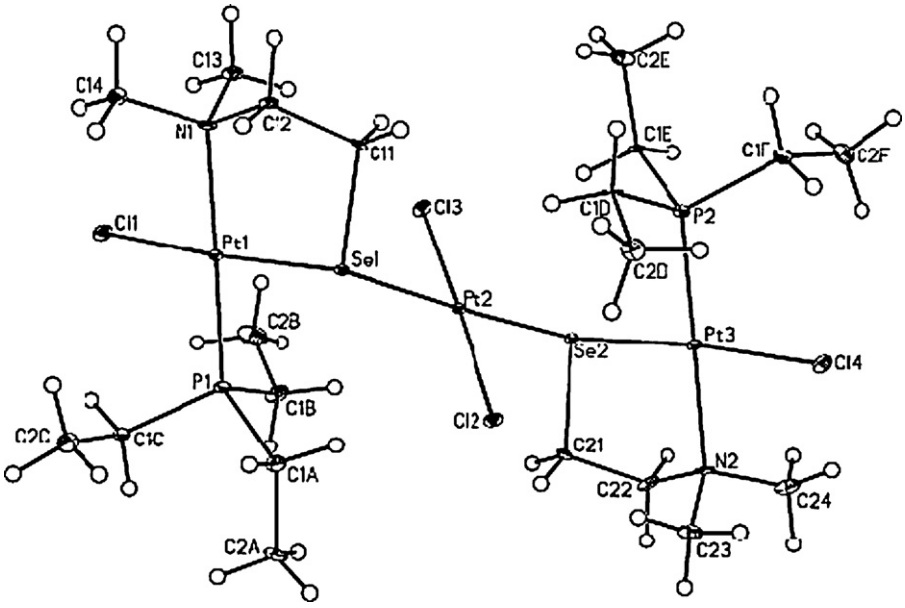


Fig. 3. Molecular structure of $[\{PtCl(SeCH_2CH_2NMe_2)(PEt_3)\}_2PtCl_2]$; [23] (Reproduced with the permission of Elsevier Ltd.).

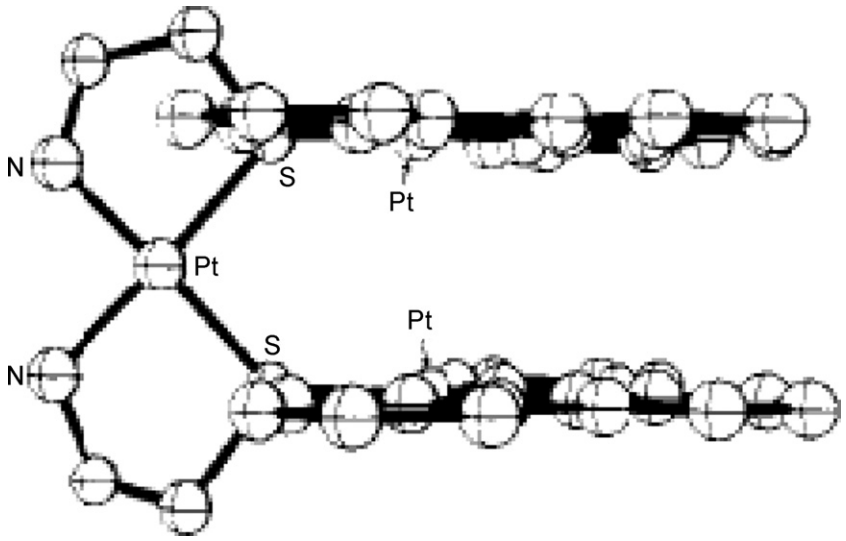
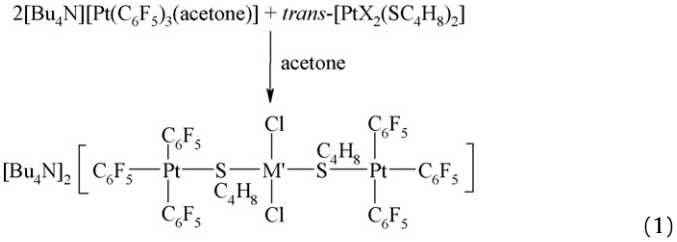
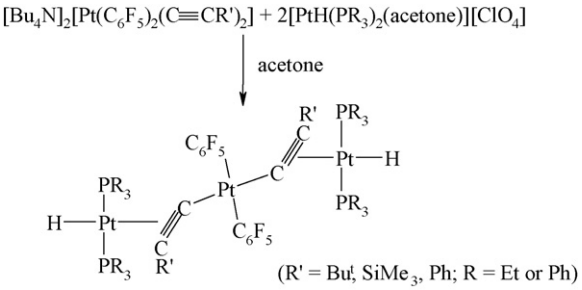


Fig. 4. Structure of $[Pt(aet)_2\{Pt(terpy)\}_2]^{4+}$; [28] (Reproduced with the permission of American Chemical Society).

tallographic center of symmetry. The terminal platinum atoms are each bonded to three C_6F_5 groups and a bridging SC_4H_8 ligand [26]. Other neutral ligands, like diynes, have also been used for constructing trinuclear complexes. Thus the reactions of $[Bu_4N]_2[Pt\{C_6F_5)_2(C{\equiv}CR')_2]$ (R′ = Bu^t, $SiMe_3$, Ph) with $[PtH(PR_3)_2(acetone)]^+$ (R = Et or Ph) yield *trans*, *trans*, *trans*-$[\{Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR')_2\}\{PtH(PR_3)_2\}_2]$ (Eq. (2)) [27]. One of the complexes, $[\{Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR')_2\}\{PtH(PEt_3)_2\}_2]$, has been structurally characterized. The alkyne ligand is asymmetrically bonded to terminal platinum atoms, the Pt–C distance being shorter with the carbon atoms bearing phenyl group [27]:



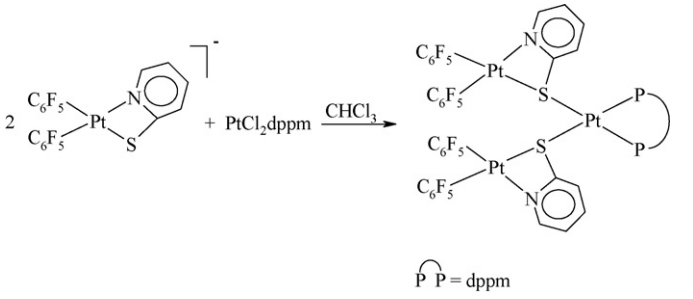
(1)



(2)

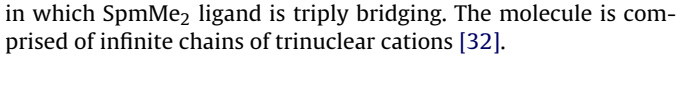
The *cis*-thiolato ligands in metal aet can bind two metal atoms to give *cis* configured trinuclear metal complexes (**IX**). Thus $M(aet)_2$ (M = Pd or Pt) reacts with $[M(terpy)X]^+$ to yield trinuclear complexes, $[M(aet)_2\{M(terpy)\}_2]^{4+}$ [28,29]. The two "M(terpy)" fragments are bridged to sulfur atoms of $M(aet)_2$ unit (Fig. 4). These fragments, mutually nearly parallel, are perpendicular to the coordination planes of the central metal atom [28,29]. Although the structures are similar, the anion in palladium complexes contribute significantly to intermolecular interactions which lead to either monomeric or polymeric forms [29].

The reaction of $[Bu_4N][Pt(C_6F_5)_2(Spy)]$ with $PtCl_2(dppm)$ in chloroform yields a trinuclear complex, $[\{Pt(C_6F_5)_2(Spy)\}_2Pt(dppm)]$ (Eq. (3)) [30]:



(3)

Reactions of trithiocarbonato complexes of palladium and platinum with $[M'(C_6F_5)_2(thf)_2]$ in dichloromethane afford trithiocarbonato-bridged trinuclear complexes (Eq. (4)) [31]:



(4)

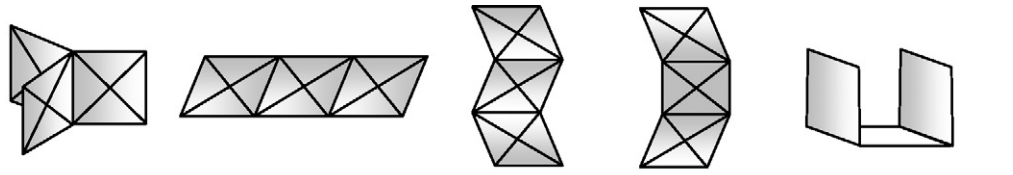
Treatment of $[Pd(\eta^3\text{-}C_4H_7)(SpmMe_2)]_2$ with KCF_3SO_3 in CH_2Cl_2 affords a trinuclear complex $[Pd_3(\eta^3\text{-}C_4H_7)_3(SpmMe_2)_2][CF_3SO_3]$ in which $SpmMe_2$ ligand is triply bridging. The molecule is comprised of infinite chains of trinuclear cations [32].

2.2. Edge-sharing trinuclear complexes

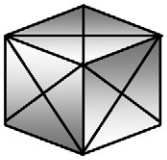
2.2.1. Single edge-bridged complexes

Trinuclear edge-sharing single-bridged complexes, $[M_3(\mu\text{-}E)_2L_4]^{2+}$ (Scheme 4, **XI**), have been isolated with chalcogenide as bridging ligands. The high nucleophilicity of chalcogenide ligand in "$M_2(\mu\text{-}E)_2$" (E = O, S, Se, Te) and flexible hinge angle (θ) of this core has allowed synthesis of numerous homo- and hetero-trinuclear complexes with predominance of sulfido-bridged derivatives. Although a variety of routes have been employed for their synthesis, the reaction of binuclear complexes, $M_2(\mu\text{-}E)_2L_4$, with a coordinatively unsaturated metal species is commonly employed.

The oxo-bridged trinuclear complexes are rare. Deprotonation of hydroxo-bridged binuclear complex, $[Pt_2(\mu\text{-}OH)_2L_4][BF_4]_2$ (L = PMe_2Ph) with strong bases, such as $LiN(SiMe_3)_2$, yields initially *cis*-$[Pt_2(\mu\text{-}O)_2L_4]{\cdot}2LiBF_4$ which decomposes in thf to give a trinuclear complex, $[Pt_3(\mu\text{-}O)_2L_6][BF_4]_2$ (Eq. (5)) [33]. Nucleophilic



(XI) single bridge **(XII)** planar **(XIII)** zig-zag or chair **(XIV)** boat **(XV)** mutually orthogonal



(XVI) Planar

Scheme 4.

attack of Cl^- at the metal atom in $[Pt_2(\mu\text{-}OH)_2L_4]^{2+}$ gives a mixture of *cis*-$PtCl_2L_2$ and $[Pt_3(\mu\text{-}O)_2L_6]^{2+}$ (L = PMe_3, PMe_2Ph) from which the latter is separated by precipitation with diethylether followed by recrystallization [34]. The ^{31}P NMR spectra show a single peak flanked by ^{195}Pt satellites with $^1J(^{195}Pt–^{31}P)$ in the range 3356–3480 Hz [33,34]. Each oxygen atom in these complexes is symmetrically coordinated to three PtL_2 fragments with Pt···Pt separation of ~2.88 Å [33,34]:

$$[Pt_2(\mu\text{-}OH)_2(PMe_2Ph)_4][BF_4]_2 + 2\ LiN(SiMe_3)_2 \downarrow [Pt_2(\mu\text{-}O)_2(PMe_2Ph)_4][LiBF_4] \downarrow [Pt_3(\mu\text{-}O)_2(PMe_2Ph)_6][BF_4]_2 \quad (5)$$

Since the first synthesis of sulfido-bridged trinuclear platinum complex, $[Pt_3(\mu\text{-}S)_2(PMe_2Ph)_6]^{2+}$ [35], a number of chalcogenido-bridged derivatives have been prepared by utilizing the ligating properties of '$M_2(\mu\text{-}E)_2$' core [36–42]. In general for their synthesis, a binuclear complex, $[M_2(\mu\text{-}E)_2L_4]$, is treated with a palladium or platinum precursor containing labile ligands (Eqs. (6) and (7)). Several other approaches have also been employed for their synthesis. For instance, reactions of MCl_2L_2 (M = Pd or Pt; L = tertiary phosphine or arsine, 1/2 substituted bipyridine) with Na_2S or NaSH [43–45] and treatment of $[M(MeCN)_4]^{2+}$ with NaEH (E = S, Se, Te) or H_2S in the presence of an appropriate phosphine (Eqs. (8) and (9)) [46–50], have been successfully used for the synthesis of chalcogenido-bridged trinuclear complexes, $[M_3(\mu\text{-}E)_2L_6]^{2+}$.

$$[M_2(\mu\text{-}S)_2L_4] + M'(C_6F_5)_2L'_2 \rightarrow [M_2M'(\mu\text{-}S)_2L_4(C_6F_5)_2] + 2L'$$
$$M = Pt,\ M' = Pd\ or\ Pt \quad (6)$$
$$L = PPh_3,\ PMe_2Ph,\ 1/2\ dppf$$

$$[Pd_2(\mu\text{-}Se)_2(dppe)_2] + [M'(MeCN)_2(dppe)]^{2+} \rightarrow [Pd_2M'(\mu\text{-}Se)_2(dppe)_3]^{2+} + 2MeCN \quad (7)$$

$$3[Pd(MeCN)_4]^{2+} + 6PR_3 + 2H_2S \rightarrow [Pd_3(\mu\text{-}S)_2(PR_3)_6]^{2+}\ \ (PR_3 = PMe_3,\ PEt_3,\ PMe_2Ph) \quad (8)$$

$$3[M(MeCN)_4]^{2+} + 2NaEH + 3P^{\cap}P \rightarrow [M_3(\mu\text{-}E)_2(P^{\cap}P)_3]^{2+}$$
$$(M = Pd,\ or\ Pt;\ E = S,\ Se,\ Te;\ P^{\cap}P = dppm,\ dppe,\ dppp,\ dppb) \quad (9)$$

High nucleophilicity of bridging chalcogenide ligand in binuclear complexes makes them susceptible to attack by halogenated solvents. Thus when binuclear sulfido-bridged complexes are dissolved in $CHCl_3$ or CH_2Cl_2, trinuclear derivatives are formed, $[M_3(\mu\text{-}S)_2(P^{\cap}P)_3]^{2+}$, conversion being too rapid for palladium complexes [44,51]. Reactions of binuclear chalcogenido-bridged complexes, $[Pt_2(\mu\text{-}E)_2L_4]$ (E = S or Se; L = PPh_3, $AsPh_3$, 1/2 dppf) with a variety of palladium and platinum substrates in methanol/acetonitrile solutions have been examined by electrospray mass spectrometry (ESMS) [52–55]. Having identified the products in the ESMS, desired complexes could be prepared in macroscopic scale and characterized by spectroscopic techniques. The sulfide ligands in arsine derivatives are less basic than the corresponding PPh_3 analogue [55]. The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $MCl_2(PPh_3)_2$ under CO atmosphere at 60 psi leads to the formation of sulfide-bridged trinuclear complexes, $[Pt_2MCl(\mu\text{-}S)_2(PPh_3)_5]^+$ (M = Pd or Pt) rather than any desulfurization or carbonylation of the precursor [56].

Oxidative addition reaction on metal(0) complexes either with chalcogens or their compounds have also been employed for the preparation of trinuclear complexes, formation of such derivatives in many instances is rather unprecedented. Treatment of $M(dppe)_2$ (M = Pd or Pt) with selenium and tellurium powder in toluene and isolation of products from dichloromethane yields trinuclear complexes, $[M_3(\mu\text{-}E)_2(dppe)_3]Cl_2$ (M/E = Pd/Se, Pt/Te) [57]. The reaction between $Pt(PPh_3)_4$ and Th_2Te_2 in dichloromethane affords an asymmetric trinuclear complex, $[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$ [58]. The reaction of $[Pt_3(CO)_6]_n^{2-}$ (n = 3–5) with PEt_3Te in THF containing Ph_4AsCl results in cluster degradation with the formation of $[Pt_2(\mu\text{-}Te)_2(PEt_3)_4]$ (80% yield), $[Pt_2(\mu\text{-}Te_2)(PEt_3)_4]^{2+}$ (2% yield) and a green–brown $[Pt_3(\mu\text{-}Te)_2(PEt_3)_6]^{2+}$ (15% yield) [59]. The latter trinuclear complex could be isolated in 70% yield by addition of $Ni(COD)_2$ to the reaction mixture containing $PtCl_2(COD)$, PEt_3Te, $TlPF_6$ [59].

Reactions of selenocarboxylate complexes, $[M(SeCOAr)_2(P^{\cap}P)]$ with $M'Cl_2(P^{\cap}P)$ in methanol in the presence of $NaBPh_4$ gives selenido-bridged homo- and hetero-trinuclear complexes in fairly

good yield (Eq. (10)) [60,61]. Treatment of $[PdCl\{S_2P(OR)_2\}PPh_3]$ with Na_2E in acetone affords neutral chalcogenido-bridged trinuclear palladium complexes in 24–42% yield (Eq. (11)) [62]. Reaction of $PdCl_2(PPh_3)_2$ with $E(SiMe_3)_2$ gives neutral chalcogenido-bridged complexes, $[Pd_3(\mu\text{-}S)_2Cl_2(PPh_3)_4]$ and $[Pd_3(\mu\text{-}Se)_2(SeSiMe_3)_2(PPh_3)_4]$ [63,64]. The former complex reacts with $As(SiMe_3)_3$ in thf to give another cluster $[Pd_9As_6(PPh_3)_8]$ [65]:

$$[M'(SeCOAr)_2(P^{\frown}P)] + 2MCl_2(P^{\frown}P) + 4\ NaBPh_4 \downarrow [M_2M'(\mu\text{-}Se)_2(P^{\frown}P)_3][BPh_4]_2$$
$$(M, M' = Pd \text{ or } Pt,\ P^{\frown}P = 2PPr_3, dppm, dppe, dppp) \quad (10)$$

$$4[PdCl\{S_2P(OR)_2\}(PPh_3)] + 2Na_2E \rightarrow [Pd_3(\mu\text{-}E)_2\{S_2P(OR)\}_2(PPh_3)_2]$$
$$(E = S \text{ or } Se,\ R = Et,\ Pr^n,\ Pr^i,\ Bu^s) \quad (11)$$

The reaction of $[Pd_2(\mu\text{-}OH)_2(C^{\frown}N)_2]$ with CS_2 in CH_2Cl_2 gives sulfido-hydroxo-bridged complexes $[Pd_3(\mu\text{-}S)(\mu\text{-}OH)(C^{\frown}N)_3]$ ($C^{\frown}N = ROC_6H_3CH{=}NC_6H_4OR$; R = Et, $C_{10}H_{21}$) [66]. The bridging hydroxo ligand can be substituted by SBu^n and O_2CEt groups on treatment with Bu^nSH and EtCOOH [66]. The reaction of $[Pd_2(\mu\text{-}SPPh_2)_2(C_6F_5)_2(PPh_3)_2]$ with $[Pd(C^{\frown}N)(acetone)_2][ClO_4]$ in refluxing acetone yields trinuclear complexes of the type $[Pd_3(\mu\text{-}SPPh_2)_2(C_6F_5)_2(PPh_3)_2(C^{\frown}N)][ClO_4]$ ($C^{\frown}N = PhN{=}NC_6H_4$, $C_6H_4CH_2NMe_2$) [67].

Deprotonation of coordinated SH group has also been used for construction of trinuclear sulfido-bridged complexes (Eqs. (12) and (13)) [68]. Reaction of $PtCl_2(dppe)$ with $Ph_2P(S)(OH)$ in refluxing toluene yields, $[Pt_3(\mu\text{-}S)_2(dppe)_3][(Ph_2PSO)_2H][OH]$ [69]. Treatment of $M_2X_2(\mu\text{-}dppm)_2$ (M = Pd, Pt; X = Cl or Br) with $[Pt(E_4)(dppe)]$ (E = S or Se) in 1:1 molar ratio after metathesis with NH_4PF_6 affords chalcogenido-bridged complexes of the type $[M_2Pt(\mu\text{-}E)_2(dppe)(EPPh_2CH_2PPh_2)_2]$ [70]:

$$Pt(SH)_2(dppp) + 2PtCl_2(COD) \rightarrow [Pt_2(\mu\text{-}S)_2(COD)_2Pt(dppp)]Cl_2 \quad (12)$$

$$2Pt(SH)_2(dppp) + PtCl_2(COD) \rightarrow [Pt_2(\mu\text{-}S)_2(dppp)_2Pt(COD)]Cl_2 \quad (13)$$

Trinuclear chalcogenido-bridged complexes have been studied by NMR spectroscopy, cyclic voltammetry, mass spectroscopy and have also been structurally characterized. The ^{31}P and ^{195}Pt NMR spectra of $[Pt_3(\mu\text{-}S)_2(PMe_2Ph)_6][BEt_4]_2$ have been analyzed and the values of $^1J(^{195}Pt{-}^{31}P) = 3202$ Hz, $^3J(^{195}Pt{-}^{31}P) = -25$ Hz and $^2J(^{195}Pt{-}^{195}Pt) = 476$ Hz have been reported [71]. The ^{31}P and ^{195}Pt resonances of $[Pt_2(\mu\text{-}S)_2L_4]$ on coordination with another metal ion result in shielding and the magnitude of $^1J(^{195}Pt{-}^{31}P)$ also increases by 175–510 Hz [38,44,68].

Photophysical properties of some sulfido-bridged bipyridine complexes have been investigated [45]. These complexes are non-emissive in solution at room temperature, but in the solid state a weak emission in the visible region is observed. These emissions have been assigned to the excited states, which have ligand field character [45].

Redox behavior of several of these complexes has been investigated by cyclic voltammetry (Eq. (14)) [42,48–50,72]. Depending on the nature of phosphine, chalcogenide ion and the metal atom, these complexes give either reversible or irreversible cyclic voltammograms. The dppe complexes in general show reversible voltammogram while dppm and dppb complexes give irreversible CV. With the same metal and phosphine ligand the ease of reduction has been in the order Te > Se > S [50]. The chemical reversibility varies in the order dppe > dppp > dppb = dppm. Substitution of dppe in $[Pd_3(\mu\text{-}E)_2(dppe)_3]^{2+}$ by dpae leads to an increase in reduction potential by ~300 mV [72]. The CV of $[Pt_2(\mu\text{-}S)_2(P^{\frown}P)_2]$ ($P^{\frown}P$ = dppe, dppp) displays two oxidation waves attributed to two one-electron oxidation of "$Pt_2(\mu\text{-}S)_2$" core with the formation of mono- and di-oxidized species, structures of which have been evaluated by DFT calculations [73]. The instability of mono-oxidized species results into the formation of trinuclear complexes, $[Pt_3(\mu\text{-}S)_2(P^{\frown}P)_3]^{2+}$ (Eq. (15)) [73]:

$$[M_3(\mu\text{-}E)_2(\overset{\frown}{P\ P})_3]^{2+} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} [M_3(\mu\text{-}E)_2(\overset{\frown}{P\ P})_3]^0 \quad (14)$$

$$[Pt_2(\mu\text{-}S)_2(P^{\frown}P)_2]^+ \rightarrow [Pt_3(\mu\text{-}S)_2(P^{\frown}P)_3]^{2+} + [Pt(S_2)((P^{\frown}P)] \quad (15)$$

A number of trinuclear chalcogenido-bridged complexes have been characterized structurally (Table 2) [39,40,44–46,49,51–56,58,59,61–63,68–72,74]. The structures of these complexes comprise of three square-planar ME_2L_2 (M = Pd or Pt, E = S, Se, Te) coordination planes sharing two μ_3-E ligands (Fig. 5). The central M_3E_2 core adopts nearly regular to distorted trigonal bipyramidal geometry. The chalcogen ligands lie above and below the M_3 triangles, which are either equilateral or isosceles (two edges long/one short or two edges short/one long). For example the palladium atoms in $[Pd_3(\mu\text{-}S)_2\{S_2P(OEt)\}_2(PPh_3)_2]$ are not equilateral as the two Pd–Pd distances (3.045 Å) are shorter than the third one (3.217 (2) Å) [62]. In the complex the two-palladium atoms are coordinated with chelating dithiophosphate groups while the third palladium atom has two PPh_3 ligands (Fig. 6).

The reactions of $[Pd_2(\mu\text{-}Spy)_2(dmp)_2]$ with $[Pd(dmp)(solv)_2][ClO_4]$ (solvent = H_2O or acetone) yields a tri palladium complex, $[Pd_3((\mu\text{-}Spy)_2(dmp)_3][ClO_4]$ in which three-palladium atoms are bridged by two Spy ligands [75]. Similarly $[Pd_3((\mu\text{-}Spy)_2(\eta^3\text{-}C_4H_7)_3][ClO_4]$ is obtained [75].

2.2.2. Double edge-bridged complexes

A variety of edge-sharing trinuclear complexes of metal atoms containing a linear array of metal atoms held together by double bridges have been isolated and characterized. These complexes have been stabilized by using Groups 15 (pyrazolate, phosphido), 16 (organochalcogenolate) and 17 (halide) ligands. The reactions of $MCl_2(pzH)_2$ (M = Pd or Pt) with various palladium and platinum substrates yield trinuclear pyrazolato-bridged complexes (Scheme 5) [76–78]. The bridging chloride in mixed pyrazolato-chloro-bridged complexes can be substituted by hydroxo or thiolato groups [77,78]. The FAB mass spectra show molecular ion peaks [78]. The molecular structure (Table 3) of $[Bu_4N]_2[Pd_3(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(C_6F_5)_4]$ revealed that the "$Pd_3(\mu\text{-}pz)_2(\mu\text{-}Cl)_2$" unit has a bent arrangement with the central palladium atom lying at the inversion center [77].

Phosphido groups are excellent bridging ligands, which due to their flexibility and stability of M–P bonds have enabled them to support a wide variety of polynuclear complexes. Thus a variety of trinuclear palladium(II) and platinum(II) complexes with bridging phosphido ligands have been isolated and characterized [79–90]. Reaction of tetranuclear complexes, $[Bu_4N]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)\}_2]$ (M = Pd or Pt) with *cis*-$PtCl_2(PPh_3)_2$ and $AgClO_4$ in 1:2:2 molar ratio yields phosphido/chloro-bridged complexes. The chloro-bridge has been substituted by hydroxo-bridges on treatment of trinuclear complexes with KOH in methanol (Scheme 6) [79]. The molecular structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(OH)_2Pt(PPh_3)_2]$ shows that the three metal planes are arranged in a boat shape structure with the dihedral angles of 12.3° and 16.2° between central palladium

Table 2
Chalcogenido-bridged trinuclear complexes characterized by X-ray diffraction.

Complex	Comments	Ref
$[Pt_3(\mu\text{-}O)_2(PMe_2Ph)_6][BF_4]_2$	Pt···Pt = 2.876 (1) (av) Å Pt–O = 2.069 (8)–2.093 (8) Å	[33]
$[Pt_3(\mu\text{-}O)_2(PMe_2Ph)_6]Cl_2$	Pt···Pt = 2.885 (1) (av) Å Pt–O = 2.078 (5)–2.094 (5) Å	[34]
$[Pd_3(\mu\text{-}S)_2(PMe_3)_6][BPh_4]_2$	Pd···Pd = 3.011 (2)–3.178 (2) Å Pd–S = 2.312 (6)–2.358 (5) Å	[46]
$[Pt_3(\mu\text{-}Te)_2(dppe)_3][BPh_4]_2$	Pt···Pt = 3.388 (2)–3.561 (1) Å Pt–Te(av) = 2.634 Å Te···Te = 3.432 (2) Å	[49]
$[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4Pt(C_6F_5)_2]$	Pt···Pt = 3.094 Å Dihedral angle between two Pt_2S_2 planes (θ) = 115.95° S···S = 3.009 Å	[40]
$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(C_6F_5)_2]$	Pt···Pt = 3.293 Å (θ) = 103.48° S···S = 2.985 Å	[40]
$[Pt_2(\mu\text{-}S)_2(dppf)_2Pd(C_6F_5)_2]$	Pt···Pt = 3.284 Å θ = 129.78° S···S = 2.983 Å	[40]
$[Pt_3(\mu\text{-}S)_2(PMe_2Ph)_6][BEt_4]_2$	Pt···Pt = 3.108 (1); 3.182 (1) Å Pt–S = 2.365 Å (av.) θ = 121.8, 116.4°	[71]
$[Pd_3(\mu\text{-}S)_2(dppe)_3]Cl_2$	Pd–S = 2.3524 (10)–2.3514 (10) Å	[51]
$[Pt_3(\mu\text{-}S)_2(dppe)_3]Cl_2$	Pt···Pt = 3.1185 (4) Å Pt–S = 2.3636 (av) Å S···S = 3.063 Å	[44]
$[Pt_3(\mu\text{-}S)_2(dppe)_3][(Ph_2PSO)_2H)][OH]$	Pt···Pt = 3.093 (3)–3.140 (3) Å Pt–S = 2.37(av) Å S···S = 3.07 Å	[69]
$[Pt_2(\mu\text{-}S)_2(dppp)_2Pt(COD)]Cl_2$	Pt–S = 2.326 (3)–2.381 (3) Å θ = 114.4–124.8°	[68]
$[Pt_2(\mu\text{-}S)_2(dppp)_2Pt(C_8H_{11})]ClO_4$	Pt–S = 2.3592 (11)–2.3789 (11) Å θ = 112.7–125.7°	[68]
$[Pd_3(\mu\text{-}S)_2(dpae)_3][BPh_4]_2$	Pd···Pd = 2.998 (2)–3.117 (3) Å Pd–S = 2.310 (5)–2.358 (4) Å S···S = 3.083 (7) Å	[72]
$[Pd_3(\mu\text{-}Se)_2(dppe)_3][BPh_4]_2$	Pd···Pd = 3.1366 (5)–3.3243 (5) Å Pd–Se = 2.4425 (5)–2.4785 (5) Å	[61]
$[Pt_3(\mu\text{-}Te)_2(PEt_3)_6]^{2+}$	Te···Te = 3.172 Å Pt···Pt = 3.577 Å Pt···Te = 2.604 Å	[59]
$[Pt_3(\mu\text{-}S)_2(dppp)_3]^{2+}$	Pt···Pt = 3.130 Å S···S = 3.024 Å Pt–S = 2.357 Å	[74]
$[Pt_2(\mu\text{-}S)_2(AsPh_3)_4Pt(COD)]^{2+}$	Pt–Pt = 3.101 (2); 3.406 (2) Å Pt–S = 2.423(av) Å	[55]
$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pt(COD)]^{2+}$	Pt···Pt = 3.045–3.323 Å Pt–S = 2.334 (2)–2.380 (2) Å	[54]
$[Pt_2(\mu\text{-}Se)_2(PPh_3)_4Pt(COD)]^{2+}$	Pt–Se = 2.4283 (10)–2.4744 (9) Å	[53]
$[Pt_2(\mu\text{-}Se)_2(COD)_2Pt(PPh_3)_2]^{2+}$	Pt–Se = 2.4392 (6)–2.4919 (6) Å	[53]
$[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(bipy)][PF_6]_2$	Pt–S = 2.3378 (8), 2.3658 (8) Å	[54]
$[Pd_3(\mu\text{-}S)_2(dppf)_2Cl_2]$	Pd···Pd = 3.13 (av) Å Pd–S = 2.274 (1)–2.369 (1) Å	[52]
$[Pd_3(\mu\text{-}S)_2(dppf)_2(PPh_3)Cl][Cl]$	Pd···Pd = 3.0572 (6)–3.2032 (7) Å Pd–S = 2.297 (2)–2.362 (2) Å	[52]
$[Pd_3(\mu\text{-}S)_2(dppf)_2(PPh_3)Cl][NO_3]$	Pd···Pd = 3.0867 (8)–3.2383 (8) Å Pd–S = 2.287 (2)–2.360 (2) Å	[52]
$[Pd_3(\mu\text{-}S)_2(Bu_2^tbipy)_3][ClO_4]_2$	Pd···Pd = 3.046 (av) Å Pd–S = 2.286 Å S···S = 2.827 (4) Å	[45]

Table 2 (*Continued*)

Complex	Comments	Ref
$[Pd_3(\mu\text{-}S)_2\{(MeOOC)_2bipy\}_3][ClO_4]_2$	Pd···Pd = 3.0749 (9)–3.156 (1) Å Pd–S = 2.278 (3)–2.302 (2) Å	[45]
$[Pt_3(\mu\text{-}S)_2(Bu_2^tbipy)_3][ClO_4]_2$	Pt···Pt = 3.145 (av) Å Pt–S = 2.303 (av) Å S···S = 2.847 (4) Å	[45]
$[Pt_2PdCl(\mu\text{-}S)_2(PPh_3)_5]^+$	M···M = 3.067 (2)–3.294 (2)	[56]
$[Pt_3Cl(\mu\text{-}S)_2(PPh_3)_5]^+$	Pt···Pt = 3.088 (1)–3.134 (1) Å Pt···S = 2.37 (av) Å	[56]
$[Pt_2(\mu\text{-}S)_2(dppp)_2PtCl_2]$	Pt···Pt = 2.942 (2), 3.277 (2) Å S···S = 2.981 Å	[39]
$[Pt_3(\mu\text{-}Te)_2(Th)(PPh_3)_5]Cl$	Pt···Pt = 3.378–3.754 Å Te···Te = 3.291 (2) Å Pt···Te = 2.630 (av) Å	[58]
$[Pd_3(\mu\text{-}S)_2\{S_2P(OEt)_2\}_2(PPh_3)_2]$	Pd···Pd = 2.9962 (14)–3.217 (2) Å Pd···S = 2.280 (3)–2.392 (2) Å	[62]
$[Pd_3(\mu\text{-}S)_2Cl_2(PPh_3)_4]$	Pd···Pd = 3.077 (3)–3.181 (4) Å Pd–S = 2.296–2.351 (2) Pd···Cl = 2.357 (3)	[63]
$[Pd_3(\mu\text{-}Se)_2(SeSiMe_3)_2(PPh_3)_4]$	Pd···Pd = 3.230 (4)–3.373 (4) Å Pd···Se = 2.434–2.499 (3) Å	[63]
$[Pd_3(\mu\text{-}S)(\mu\text{-}SBu^n)(C^{\frown}N)_3]$ (C–N = $EtOC_6H_3CH{=}NC_6H_4OEt$)	Pd···Pd = 3.047–3.387 Å Pd–S = 2.304 (2)–2.430 (3) Å	[66]
$[Pd_3(\mu\text{-}S)(\mu\text{-}O_2CEt)(C^{\frown}N)_3]$ ($C^{-}N$ = $EtOC_6H_3CH{=}NC_6H_4OEt$)	Pd···Pd = 3.145–3.500 Å Pd–S = 2.254–2.296 (2) Å Pd–O = 2.195 (5)–2.237 (5) Å	[66]
$[Pd_3(\mu\text{-}SPPh_2)_2(C_6F_5)_2(PPh_3)_2(C^{\frown}N)][ClO_4]$	$SPPh_2$ acts as a bridging ligand	[67]
$[Pd_3(\mu\text{-}Spy)(dmp)_3][ClO_4]$	Pd···Pd = 2.956 (4)–2.958 (4) Å	[75]
$[PtPd_2((\mu\text{-}Se)_2(dppe)(SePPh_2CH_2PPh_2)_2]$	Pd–Se = 2.413 (1)–2.458 (1) Å	[70]

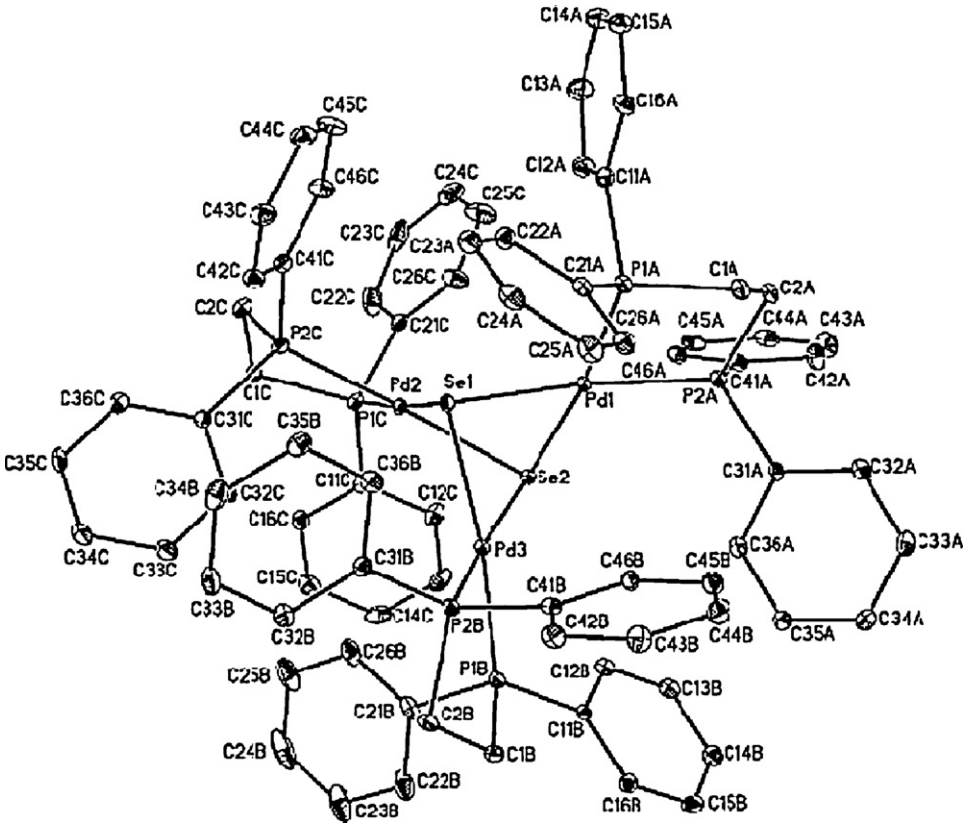


Fig. 5. Molecular structure of $[Pd_3(\mu\text{-}Se)_2(dppe)_3]^{2+}$; [61] (Reproduced with permission of Elsevier Ltd.).

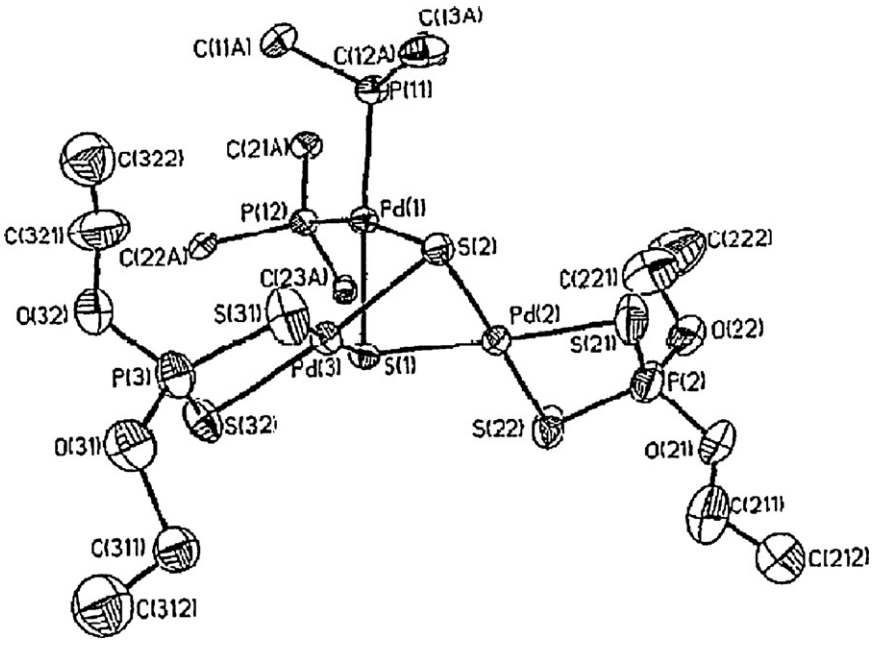


Fig. 6. Molecular structure of $[Pd_3(\mu\text{-}S)_2\{S_2P(OEt)_2\}_2(PPh_3)_2]$; [62] (Reproduced with permission of Elsevier Ltd.).

$$2[Pd(acac)(\eta^3\text{-allyl})] + PdCl_2(pzH)_2 \longrightarrow 2[Pd_3(\mu\text{-pz})_2(\mu\text{-Cl})_2(\eta^3\text{-allyl})_2] + 2acacH$$
(allyl = C_3H_5 or C_4H_7)

$$2[Bu_4N][M(C_6F_5)_2(acac)] + M'Cl_2(pzH)_2 \longrightarrow 2[Bu_4N]_2[M_2(C_6F_5)_4(\mu\text{-pz})_2(\mu\text{-Cl})_2M'] + 2acacH$$
(M = Pd or Pt; M' = Pd or Pt)

$$2[PdCl(acac)(PPh_3)] + PdCl_2(pzH)_2 \longrightarrow [Pd_3(\mu\text{-pz})_2(\mu\text{-Cl})_2Cl_2(PPh_3)_2]$$
$$\downarrow 2\ NaSR'$$
$$[Pd_3(\mu\text{-pz})_2(\mu\text{-SR'})_2Cl_2(PPh_3)_2]$$

$$[Pd_2Ph_2(\mu\text{-OH})_2(PR_3)_2] + PdCl_2(pzH)_2 \longrightarrow [Pd_3Ph_2(\mu\text{-Cl})_2(\mu\text{-pz})_2(PR_3)_2] + 2\ H_2O$$
$$\downarrow 2\ NaSR' / Pb(SR')_2$$
$$[Pd_3Ph_2(\mu\text{-SR'})_2(\mu\text{-pz})_2(PR_3)_2]$$
(R = Ph or tol; R' = Ph, ClC_6H_4, C_6F_5.)

Scheme 5.

$$[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M[(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2] + 2\ PtCl_2(PPh_3)_2 + 2\ AgClO_4$$
$$\downarrow$$
$$2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$$
$$\downarrow KOH$$
$$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)_2Pt(PPh_3)_2]$$
(M = Pd or Pt)

Scheme 6.

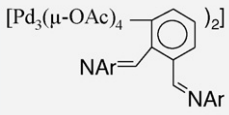
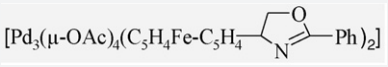
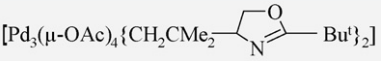
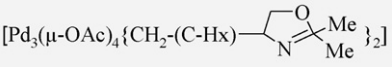
and terminal platinum coordination planes [79]. When hydroxo-bridged complexes are treated with HX, the X-bridged complexes, $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}X)_2Pt(PPh_3)_2]$ (X = Cl, Br, SPh) are formed exclusively [79].

Treatment of *cis*-$[M(C_6F_5)_2(PPh_2)_2]^{2-}$ (prepared *in situ* by a reaction between *cis*-$[M(C_6F_5)_2(PPh_2H)_2]$ and BuLi) with $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(PPh_3)]$ (a 30 electron complex) in 1:1 molar ratio in the presence of Bu_4N^+ affords trinuclear phosphido-bridged complexes, $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]^{2-}$ (M = Pd or Pt; M′ = Pd or Pt) (Fig. 7) [81]. These complexes can also be obtained by a reaction between *cis*-$[M(C_6F_5)_2(PPh_2)_2]^{2-}$ and *trans*-$PdCl_2(tht)_2$ or *cis*-$[PtCl_2(MeCN)_2]$ in a 2:1 ratio [81]. The triplatinum complex is oxidized by $AgClO_4$ to a species containing platinum in oxidation state of 2.67 (two platinum in III and one in II) [81]. In the complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ two platinum atoms are linked by a Pt–Pt bond which is also stabilized by phosphido-bridges [81]. The trinuclear complex $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ reacts with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in 1:2 ratio in dichloromethane to yield a binuclear complex, $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ and a tetranuclear derivative, $[Bu_4N][Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_5]$ [83]. The reaction of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^{2-}$ with iodine in 1,2-dichloroethane at room temperature and at reflux gives a Pt–Pt bonded trinuclear complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ and a platinum complex, $[(C_6F_5)(PPh_2C_6F_5)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^-$, respectively [84]. The reaction of two equivalents of iodine with a trinuclear cluster $[Pt_3(\mu\text{-}PPh_2)_3(PPh_3)_3]$ yields a yellow air stable iodo-/phoshido-bridged complex, $[Pt_3(\mu\text{-}I)_2(\mu\text{-}PPh_2)_2I_2(PPh_3)_2]$ [86].

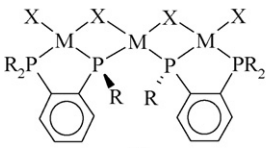
Table 3
Trinuclear edge-sharing palladium and platinum complexes characterized by X-ray crystallography.

Complex	Comment	Reference
$[Bu_4N]_2[Pd_3(C_6F_5)_4(\mu\text{-}Cl)_2(\mu\text{-}pz)_2]$	Pd–N = 2.001 (3), 2.076 (3) Å	[77]
$[(C_6F_5)_2Pt(\mu\text{-}PPh)_2)_2Pd(\mu\text{-}OH)_2Pt(PPh_3)_2]$	Pt–Pd = 3.273 (1), 3.562 (1) Å boat shape structure	[79]
$[PPN]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$	Central platinum atom lies at the inversion center; Pt···Pt = 3.592 (1) Å	[81]
$[(C_6F_5)(Ph_2C_6F_5P)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^-$	Pt···Pt = 3.600 (1), 3.477 (1) Å	[84]
$[(C_6F_5)(Ph_2C_6F_5P)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt\ (\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^-$	Pt···Pt = 3.577 (1) Å	[84]
$[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)\}_2Pt]$	Pt.Pt = 3.512 (1), 3.655 (1) Å; Pt–I = 2.66281 (9)–2.6962 (8) Å; Pt_3 core has a chair arrangement	[87]
$[\{(PEt_3)HPt(\mu\text{-}PPh_2)_2\}_2Pt]$	Linear arrangement with Pt···Pt separation of 3.572 (1) Å	[89]
$[(+)_\delta\text{-}L_2Pd_3Cl_4]$	Chair conformation Pd···Pd = 3.223, 3.157 Å	[90]
$[(+)_\delta\text{-}L_2Pd_3Br_4]$	Chair conformation Pd···Pd = 3.156, 2.934 Å	[90]
$[(+)_\delta\text{-}L_2Pt_3Cl_4]$	Chair conformation Pt···Pt = 3.135, 3.206 Å	[90]
$[(+)_\delta\text{-}L_2Pt_3Br_4]$	Chair conformation, Pt···Pt = 3.216 Å Boat conformation, Pt···Pt = 3.258 Å	[90]
$[(C_4H_7)Pd(\mu\text{-}SMes)_2Pd(\mu\text{-}SMes)_2Pd(C_4H_7)]$	Central Pd at inversion center, zig-zag shape, thiolates in *anti* arrangement Pd–S = 2.39 (av) Å	[17]
$[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(PPr_3)_2]$	Zig-zag shape of $Pd_3(\mu\text{-}SeR)_4$ fragment, Pd···Pd = 3.352, 3.204 (1) Å Pd···Se = 2.4004 (15)–2.4803 (16) Å	[91]
$[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOH)_4(PPr_3)_2]$	Boat conformation of $Pd_3(\mu\text{-}SeR)_4$ core; R groups on Se adopt an *anti* configuration; carboxylic group forms hydrogen bonded supra-molecular 2D net work; Pd···Pd = 3.1757 (13) Å	[92]
$[Pd_3(\mu\text{-}ScHx)_4Cl_2(PMe_3)_2]\cdot CHCl_3$	Pd···Pd = 3.234 (2), 3.230 (2) Å Pd–S = 2.294 (2)–2.4000 (2) Å Zig-zag shape	[93]
$[Pd_3(\mu\text{-}SC_6H_4S\text{-}1,2)_2C_6H_4STbt)_2(PPh_3)_2]$	Pd–S = 2.2873, 2.2798 (10) Å Pd···Pd = 3.194 Å	[95]
$[Pt_3(\mu\text{-}Stol)_4(dppm)_2][CF_3SO_3]_2\cdot 6CH_2Cl_2$	Pt···Pt = 3.264 (5)–3.315 93) Å Pt–S = 2.292 (6)–2.364 (5) Å Zig-zag shape with thiolates in *anti* configuration	[97]
$[Pd_3(\mu\text{-}SCH_2C_5H_9N)_4]Cl_2$	Pd–S = 2.283 (4)–2.322 Å Pd···Pd = 3.217 (1) Å	[99]
[Pd$_3${bis(α,α′-(2-mercapto-5-methyl benzene-1,3-diyl)di(methylidyne)di(azino)bis(cyclohexanemethanol)ato(3−)]	Pd···Pd = 3.5386 (7), 3.5633 (6) Å Pd–S = 2.209 (1)–2.285 (2) Å	[101]
$[Pt_3(\mu\text{-}SNCPhNS)_2(PPh_3)_4]$	Pt···Pt = 2.865 (1) Å Pt–S = 2.332 (5)–2.387 (4) Å linear Pt_3 chain	[103]
$[Pd_3(\mu\text{-}SNCPhNS)_2(PPh_3)_4]\cdot 2CH_2Cl_2$	Pd···Pd = 2.8499 (11), 2.8693 (2) Å Pd–S = 2.332 (2)–2.402 (3) Å linear Pd_3 chain	[103]
$[Pd_3(\mu\text{-}SNC)(4\text{-}MeC_5H_4N)NS)_2(PPh_3)_4]$	Pd···Pd = 2.852 (1) Å Pd–S = 2.337 (3)–2.388 (3) Å zig-zag Pd_3 core	[104]
$[Pd_3(\mu\text{-}SNC)(Et_3B\text{-}NC_5H_4Me\text{-}4)NS)_2(PPh_3)_4]$	Pd···Pd = 2.8638 (5) Å Zig-zag Pd_3 core	[104]
$[Pd_3(\mu\text{-}SNC)(Et_3B\text{-}NC_5H_4Me\text{-}3)NS)_2(PPh_3)_4]$	Pd···Pd = 2.884 (1) Å Zig-zag Pd_3 core	[104]
$[Pd_3\{SP(O)NHBu^t)_2\}_4\{SP(O)(NHBu^t)_2]$	Pd···Pd = 3.501 Å; Pd–S = 2.322(av) Å	[105]
$[Pt\{S_2C_2N_2(CHMePh)_2\}_2\{Pd(C_3H_5)\}_2]$	Bent configuration	[106]
$[Pd_3(SCH_2CH_2CH_2S)_2(dppp)_2]^{2+}$	Pd···Pd = 3.0935 (8) Å	[107]
$[Pd_3(donp)_2(bipy)_3]\{PF_6\}_2$	Pd···Pd = 2.803 (2) Å	[108]
$[Pt_3(donp)_2(bipy)_3]\{PF_6\}_2$	Pt···Pt = 2.804 (2) Å	[108]
$[Bu_4N]_2[Pd_3Cl_8]$	Pd–Cl = 2.255 (5)–2.349 (5) Å	[110]
$[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2(C_6F_5)_2]$	Pt···Pt = 3.494 Å Pt.Cl = 2.313 (2)–2.441 (2) Å Pt_3Cl_4 core slightly distorted	[111]
$[Pd_3(\mu\text{-}Cl)_4(\eta^3\text{-}C_4H_7)_2]$	Pd–Cl = 2.297 (9)–2.418 (9) Å	[112]

Table 3 (*Continued*)

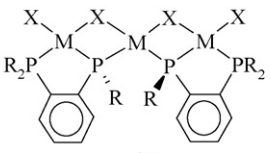
Complex	Comment	Reference
	Pd_3Cl_4 unit has a flat rippled appearance	
$[Pd_3(\mu\text{-}Cl)_4\{\eta^3\text{-}C_4Bu^t{}_3(H)CH_2Cl\}_2]$	Pd–Cl = 2.300 (2)–2.488 (3) Å Pd_3Cl_4 fragement is bent	[114]
$[Pd_3(\mu\text{-}OAc)_4\{\eta^3\text{-}C_3H_3(OCBu^t)_2\}_2]$	Pd···Pd = 2.864 (1) Å Pd–O = 1.998 (8)–2.105 (6) Å	[116]
$[Pd_3Ph_2(\mu\text{-}OAc)_4(SbPh_3)_2]$	Pd···Pd = 3.01 (3) Å Pd–O = 1.942 (27)–2.181 (26) Å	[117]
$[Pd_3(\mu\text{-}Cl)_4Cl_2(TRIP)_2]$	Pd–Cl = 2.2782 (14)–2.4214 (15) Å	[125]
 Ar = 2,6-$Pr^i2C_6H_3$	Pd–O = 2.057 (4), 2.127 (4) Å Pd···Pd = 2.9721 (6) Å $Pd_3(OAc)_4$ has a 'S' shape configuration	[131]
$[Pd_3(\mu\text{-}OAc)_4\{C_5H_4Re(PPh_3)(NO)(CH_2PPh_2)\}_2]$	Pd···Pd = 2.9292 (8)–2.9452 (5) Å	[130]
	Pd···Pd = 3.0457 (5) Å	[128]
		[129]
		[129]
[(nacnac)Pd(μ-Cl)(μ-$NHC_6H_4Bu^t$-4)Pd(nacnac)$PdCl_2(NH_2C_6H_4Bu^t$-4]	Pd–N = 2.100 (5), 2.087 (9) Å	[134]
nacnac=PhN=C(Me)CH_2C(Me)=NPh	Pd–Cl = 2.3351 (19), 2.3941 (18) Å	
$[Bu_4N]_2[(C_6F_5)_2Pt(C{\equiv}CPh)_2Pt(C{\equiv}CPh)_2\ Pt(C_6F_5)_2]$	Pt···Pt = 3.400 (1), 3.429 (1) Å Non-planar "$Pt_3(C{\equiv}Ph)_4$" core	[135]
$[Pt(\mu\text{-}C{\equiv}CPh)_2(\mu\text{-}dmpz)_2\{Pt(C,P)\}_2]$	Pt···Pt = 3.213 (5), 3.256 (1) Å Pt–N = 2.054 (5)–2.089 (5) Å Terminal platinum planes are perpendicular to the central platinum plane	[138]
$[Pt(\mu\text{-}S)(\mu\text{-}SBz)_3(PPh_3)_3]Cl$	Pt–S = 2.363 (av) Å Pt–P = 2.259–2.271 Å	[139]
$[Pt(\mu_3\text{-}Se)(\mu_3\text{-}SePh)_3PPh_3)_3]Cl$		[140]

Treatment of *cis*-$[Pt(X_6F_5)_2(PPh_2H)_2]$ with $[Pt(C_7H_{10})_3]$ and PPh_3 in 1:1:1 ratio in toluene affords hydrido-bridged bi-, $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_2H)_2]$ and trinuclear, $[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)\}_2Pt]$ in 36 and 21% yields, respectively [87]. The core of the latter complex is planar with Pt–Pt bonds (2.874 (1); 2.852 (1) Å) [87]. This complex on treatment with iodine in dichloromethane yields an iodo-bridged derivative, $[\{(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)\}_2Pt]$ which has a chair arrangement of the trinuclear skeleton with the terminal platinum atoms planes forming dihedral angles of 42.0° and 19.9° with the central metal atom plane [88]. The reaction of $[Pt(PEt_3)_3]$ with PPh_2H in 1:2 molar ratio yields a linear trinuclear platinum complex with terminal hydrido-ligands, $[\{(PEt_3)HPt(\mu\text{-}PPh_2)_2\}_2Pt]$ [89]. The latter is isolated as a mixture of *syn* and *anti* isomers, the structure of the *anti* form has been established by X-ray crystallography. The ^1H NMR spectrum displays hydrido signals at δ −5.83 (*anti* isomer, $^1J(Pt–H) = 1032$ Hz) and −6.10 (*syn* isomer, $^1J(Pt–H) = 1036$ Hz) [89]. During recrystallization of $[(+)\text{-}LH]MX_2$ (M = Pd or Pt; X = Cl or Br) yellow to red crystals of trinuclear complexes $[(+)_\delta\text{-}L_2M_3X_4]$ (LH = P,P,P′-tris(+)9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene) have been isolated. The bridging and terminal halides are oriented on one side. With such arrangements, three possible stereo isomers (**2**–**4**) have been isolated and structurally characterized [90]. Both chair and boat configurations for the three square-planar metal atoms have been identified.



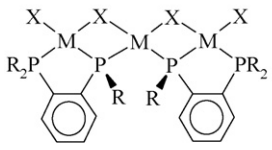
(2)

M,X = Pd, Cl; Pd, Br; Pt,Cl;Pt, Br



(3)

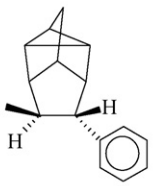
M,X = Pd, Cl; Pd, Br; Pt,Cl



(4)

M,X = Pt, Br

R =



Double-bridged edge-sharing trinuclear complexes containing organochalcogenolates have been synthesized and characterized.

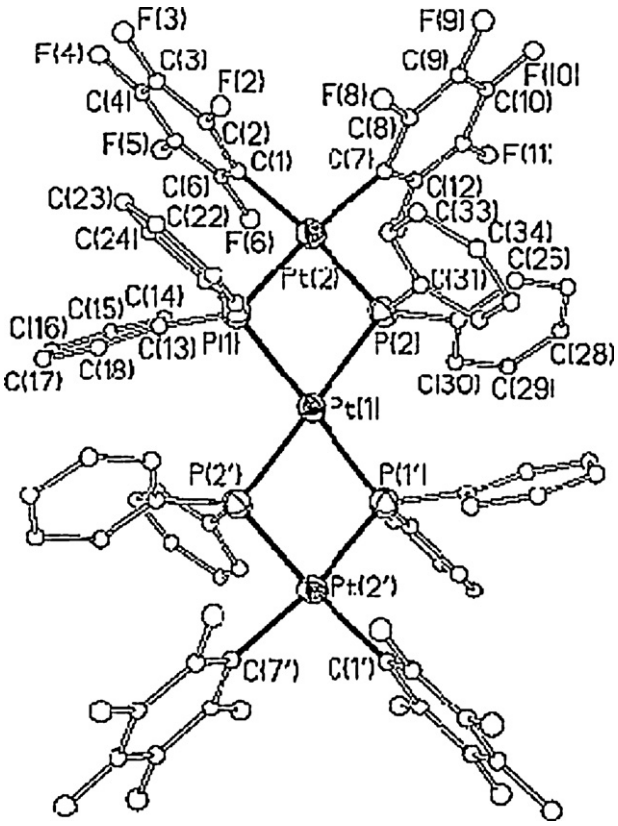
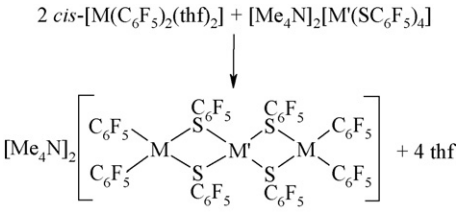


Fig. 7. Structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^{2-}$; [81] (Reproduced with permission of American Chemical Society).

All the three structural motifs (planar, chair and boat) have been identified. The M···M separation in these complexes reduces significantly from those containing phosphido-bridges. Formation of several such complexes [17,91–94] often takes place by the reaction of a homeleptic palladium chalcogenolate complex, $Pd(ER)_2$, generated *in situ* by cleavage of other auxiliary ligands on palladium, with a binuclear chalcogenalato bridged palladium complex. In fact this has been demonstrated by isolation of $[(C_4H_7)Pd(\mu\text{-}SMes)_2Pd(\mu\text{-}SMes)_2Pd(C_4H_7)]$ by a reaction between $[Pd(SMes)_2]_n$ and $[(C_4H_7)Pd(\mu\text{-}SMes)_2Pd((C_4H_7)]$ in refluxing dichloromethane. In several cases when binucler complexes are left in solution for recrystallization a small amount of orange to red crystals of trinuclear complexes, *e.g.*, $[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOMe)_4(PPr_3)_2]$ [91], $[\{(C_4H_7)Pd(\mu\text{-}SMes)_2\}_2Pd]$ [17], are formed. In other cases trinuclear complexes are formed by the reaction of a dinuclear palladium complex with mercaptan. Thus the reaction of $[Bu_4N]_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ with excess of ethylmercaptan and 1,2-benzenedithiol in methanol under refluxing and at RT, respectively yield trinuclear complexes, $[Bu_4N]_2[(C_6F_5)_2Pd(\mu\text{-}SEt)_2Pd(\mu\text{-}SEt)_2Pd(C_6F_5)_2]$ and $[Bu_4N][\{(C_6F_5)_2Pd(S_2C_6H_4)\}_2Pd]$ [94]. Similarly, reaction of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2]$ with excess of cyclohexyl mercaptan in refluxing chloroform yields a trinuclear complex $[Pd_3Cl_2(\mu\text{-}SHx)_4(PMe_3)_2]$, but the reaction at room temperature affords the expected binuclear complex, $[Pd_2Cl_2(\mu\text{-}SHx)_2(PMe_3)_2]$ [93]. Oxidative addition of diorganodisulfides on $Pd(PPh_3)_4$ has been known to yield binuclear complexes, $[Pd_2((\mu\text{-}SR)_2SR_2(PPh_3)_2]$. However, bulky hexathio ether containing a disulfide bond reacts with $Pd(PPh_3)_4$ via a three-step palladium insertion reaction (one S–S– and two C–S bonds), to yield a trinuclear complex, $[Pd_3(\mu\text{-}SC_6H_4S\text{-}1,2)_2(C_6H_4STbt)_2(PPh_3)_2]$ [95]. Reaction of $M(C_6F_5)_2(thf)_2$ with $[M(SC_6F_5)_4]^{2-}$ (Eq. (16)) has been employed to prepare homo- and hetero-trinuclear palladium and platinum complexes [96]:



M = M' = Pd or Pt
M = Pd; M' = Pt
M = Pt; M' = Pd (16)

Treatment of $PtCl_2(RCN)_2$ with $[Pt(SR)_2(dppm)]$ (R = Et, Ph, tol, 4-ClC_6H_4) in 1:2 ratio in the presence of $NaBF_4$ or $Tl(CF_3SO_3)$ gives thiolato-bridged trinuclear complexes (Eq. (17)). The FAB mass spectra show peaks due to $[M-X]^+$ and $M-2X^+$. The spectrum of $[Pt_3(\mu\text{-}SPh)_4(dppm)_2]^{2+}$ also exhibits peaks due tetranuclear com-

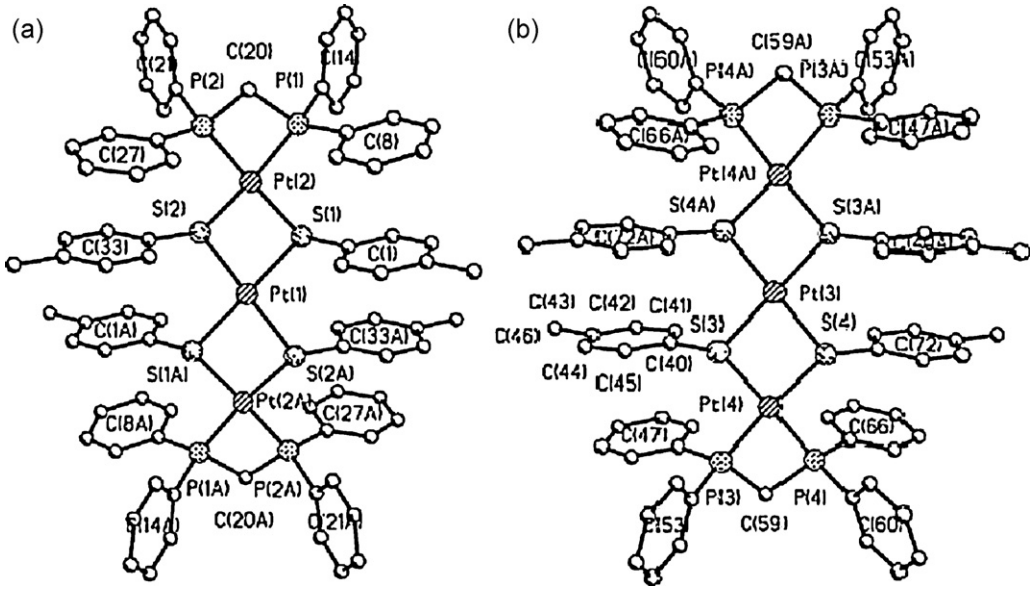


Fig. 8. (a) Molecular structure of $[Pt_3(\mu\text{-}Stol)_4(dppm)_2]^{2+}$, (b) perspective view of the molecule showing an *anti* arrangement of Stol groups.; [97] (Reproduced with permission of Elsevier Ltd.).

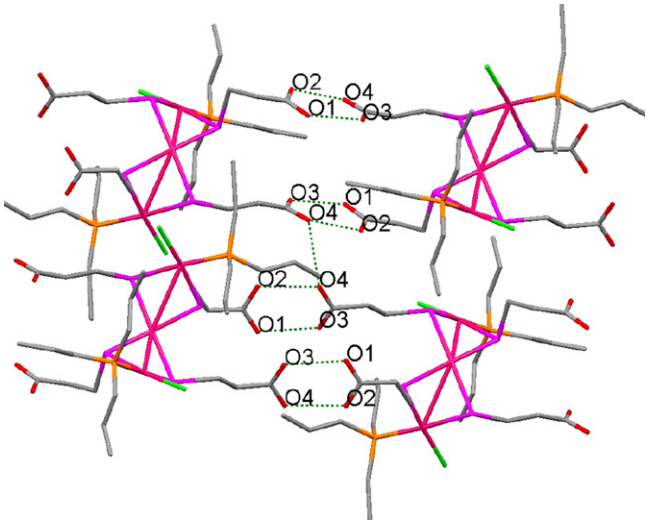
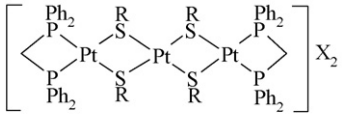


Fig. 9. Hydrogen bonding interactions in trans-$[Pd_3Cl_2(\mu\text{-}SeCH_2CH_2COOH)_4(PPr_3)_2]$; [92] (Reproduced with permission of Elsevier Ltd.).

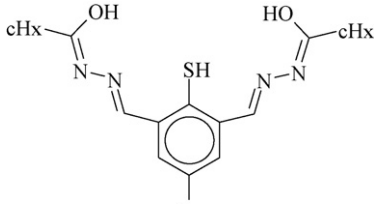
plex [97]. The complex, $[Pt_3(\mu\text{-}Stol)_4(dppm)_2][CF_3SO_3]_2{\cdot}6CH_2Cl_2$ has a zig-zag shape with thiolato ligands in *anti* arrangement (Fig. 8). When R groups on chalcogen atoms have OH groups, as in $[Pd_3(\mu\text{-}SeCH_2CH_2COOH)_4(PPr_3)_2]$, supra-molecular aggregation through a series of OH···O=C contacts (2.69 Å) has been observed which leads to a 2D structure (Fig. 9) [92]:

$$PtCl_2(RCN)_2 + 2\ Pt(SR')_2(dppm) + 2NaBF_4\ /2Tl(CF_3SO_3)$$



X = BF_4 or CF_3SO_3
R = Et, Ph, tol, 4-ClC_6H_4 (17)

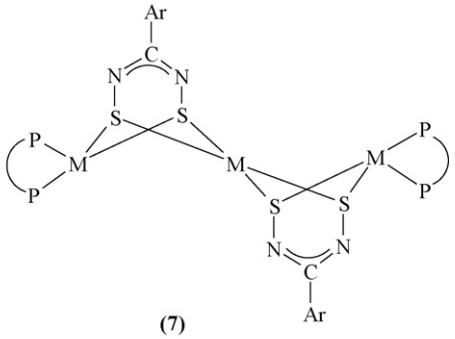
Reaction of Na_2PdCl_4 with 3-(mercaptomethyl)piperdine dissolved in aqueous ammonia, yields a trinuclear complex, $[Pd_3L_4]Cl_2{\cdot}2H_2O$ (L = $SCH_2C_5H_9N$) [98]. The central palladium has a planar PdS_4 core while the terminal palladium atoms have chelated thiolato ligand with *cis*-S_2PdN_2 environment. There is a folding along the S–S axis of the four-membered PdS_2Pd rings [98,99]. In a similar approach a platinum complex, $[Pt_3(ttz)_8][Cl]_6$ was prepared by the reaction of K_2PtCl_4 and ttzH in water and decomposing the mixture of mononuclear complexes, $Pt(ttz)_2Cl_2$ and $[Pt(ttz)_3Cl]Cl$ at 100 °C under nitrogen [100]. All the three platinum atoms have PtS_4 core. Trinuclear palladium complex, Pd_3L_2 (LH_3 = **5**), has been prepared and structurally characterized [101].



(5)

Reactions of 1,2,3,5-dithiadiazoles (**6**) with M^0 compounds, $Pt(PPh_3)_3$ or $Pt(PPh_3)_4$, $Pd(PPh_3)_4$ and a mixture of $Pd_2(dba)_3$ and dppf, result into ring opening reaction by reductive clearage of S–S bond of dithiadiazole and yield trinuclear complexes, **7** [102–104]. The central metal atom has a MS_4 core while the terminal metal atoms have a P_2S_2 coordination environment. These complexes have a linear M_3 chain.

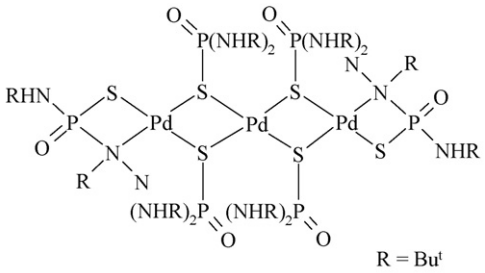
(6)



(7)

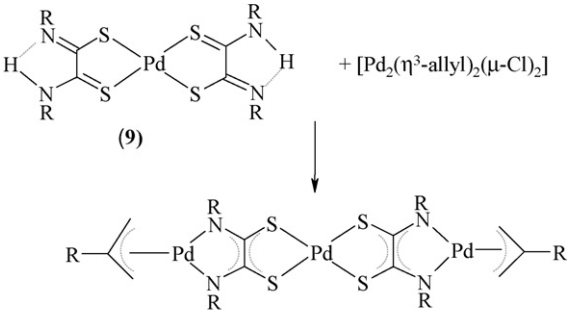
M = Pd or Pt; P P = $2PPh_3$, dppf
Ar = Ph, 4-Mepy, 3-Mepy

Treatment of sodium salt of diamidothiophosphoric acid with *trans*-$PdCl_2(MCN)_2$ in acetonitrile affords a trinuclear palladium complex (**8**) [105]. Platinum dithioxamide complex (**9**) has been employed for the preparation of trinuclear complexes (**10**) (Eq. (18)) [106].



(8)

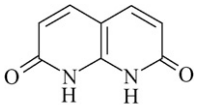
R = Bu^t



(9)

(10) (18)

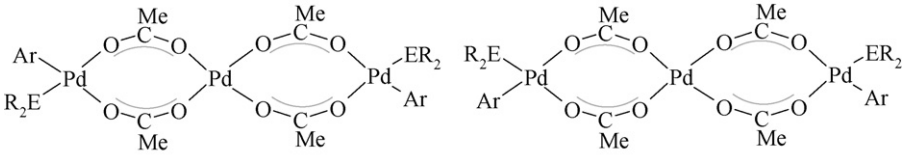
Treatment of [Pd(dppp)($SCH_2CH_2CH_2S$)] with elemental selenium in 1:1 ratio in the presence Me_4NCl affords a cationic trinuclear complex, $[Pd_3(\mu\text{-}SCH_2CH_2CH_2S)_2(dppp)_2]^{2+}$ [107]. Reactions of MCl_2(bipy) with 1,8-naphthylpyridin-2,7-dione (H_2donp) (**11**) and LiOH in the presence of NH_4PF_6 afford *cis*-$[M_3(donp)_2(bipy)_3][PF_6]_2$ (M = Pd or Pt) in which three metal centers are bridged linearly by two donp ligands [108,109].



H_2donp

(11)

The chloro-bridged trinuclear complexes have been isolated. The reaction of $PdCl_2$ with $[Bu_4N][Re{\equiv}N(Cl)_4]$ in thf gives orange



Scheme 7.

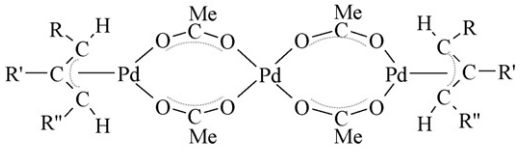
crystals of a trinuclear complex, $[Bu_4N]_2[Pd_3Cl_8]$ together with some crystals of $[Bu_4N]_2[\{(thf)Cl_4Re{\equiv}N\}_2PdCl_2]$ [110]. The former has slightly asymmetric chloro-bridges and each palladium is coordinated to four chloride ligands [110]. The complexes containing other ligands on terminal palladium atoms have also been prepared. Thus the reaction of $[R_4N]_2[M'Cl_4]$ with *cis*-$[M(C_6X_5)_2(thf)_2]$ in 1:2 molar ratio yields trinuclear complexes (Eq. (19)) [111]. The X-ray structural analysis of $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ revealed that the central platinum atom is coordinated with four chlorides and resides at the center of symmetry. The square planes of terminal platinum atoms make a dihedral angle of 6° with the central platinum square plane [111]:

$$[R_4N]_2\,[M'Cl_4] + 2\ cis\text{-}[M(C_6X_5)_2(thf)_2] \longrightarrow [R_4N]_2\,[(C_6X_5)_2M(\mu\text{-}Cl)_2M'(\mu\text{-}Cl)_2M(C_6X_5)_2]$$

(M = M' = Pd or Pt; X = F or Cl; R = Me or Bu) (19)

Trinuclear allylpalladium complexes containing chloro-bridges, $[Pd_3(\mu\text{-}Cl)_4(\eta^3\text{-ally})_2]$ (allyl = C_4H_7, $C_4Bu^t_3(H)CH_2Cl$, C_7H_8MeCl) have been prepared by the reactions of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with $[PdCl_2(PhCN)_2]$ in a variety of solvents [112–114]. The η^3-cyclobutenyl complex can also be prepared by the reaction of $PdCl_2(PhCN)_2$ with 1,2,3-tri-*tert*-butyl-3-vinyl-1-cyclopropene in 1:1:1 ratio in dichloromethane [114]. The central palladium atom in these complexes lies at the inversion center and is coordinated by four bridging chloride ligands.

Reactions of $[Pd(OAc)_2]_3$ with mono olefins (*e.g.*, cyclohexene, hex-1-ene, *cis*-hex-2-ene, oct-1-ene, *cis*-pent-2-ene, propene and 2,3,3-trimethylbut-1-ene) in acetic acid afford acetato-bridged trinuclear allylpalladium complexes, $[Pd_3(\mu\text{-}OAc)_4(\eta^3\text{-allyl})_2]$ (**12**) [115]. These complexes are fluxional as acetato-bridges allow inter-conversion of different conformations of the allyl groups. Palladium acetate when treated with 2,6-disubstituted pyrylium salts in refluxing acetic acid in the presence of aqueous sodium acetate, trinuclear bis(acylallyl)palladium acetates, $[Pd_3(\mu\text{-}OAc)_4\{\eta^3\text{-}C_3H_3(COR)_2\}_2]$ are formed [116]. Palladium acetate reacts with tripheylantimony in THF-dioxane mixture at 45 °C to give $[Pd_3Ph_2(\mu\text{-}OAc)_4(SbPh_3)_2]$ which has been structurally characterized [117].

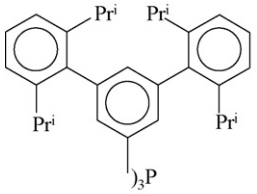


(12)

Activation of arene C–H bond by palladium acetate–dialkylsulfide systems has been reported [118–121]. In these reactions trinuclear arylpalladium acetate-bridged complexes, $[Pd_3Ar_2(\mu\text{-}OAc)_4(SR_2)_2]$ (R = Et, Pr^i, Bu^i), are formed. Although several arenes such as benzene, *p*-xylene, are activated by palladium acetate-dialkysulfide systems, compounds like toluene, *o*- and *m*-xylenes yield coupling products (biaryls) instead. However, the latter arenes are activated by palladium acetate-dipropylselenide system to give desired trinuclear arylpalladium complexes, $[Pd_3Ar_2(\mu\text{-}OAc)_4(SePr_2)_2]$ [122]. In these reactions both *al* and *ak* isomers are formed (Scheme 7). Various positional isomers have also been indentified from substituted benzenes [120,122]. The structure of $[Pd_3(C_6H_3Me_2\text{-}2,5)_2(\mu\text{-}OAc)_4(SBu^i_2)_2]$ (*al* isomer) shows that the central palladium atom, coordinated to four bridging acetate ligands, lies on the inversion centre with Pd···Pd separation of 2.979 (1) Å [123]. The dihedral angle between the square planes of palladium atom is 32.1° indicating that these planes deviate significantly from parallel arrangement [123].

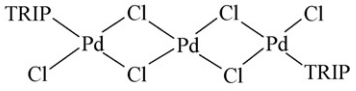
The tetranuclear cluster, $[Pd(\mu\text{-}NO)(\mu\text{-}O_2CR)]_4$ (R = CF_3, CCl_3) formed by replacement of CO by NO in $[Pd_2((\mu\text{-}CO)_2(\mu\text{-}O_2CR)_2]_n$, when dissolved in aromatic solvents under a NO atmosphere, yields trinuclear nitrosyl complexes, $[Pd_3(\mu\text{-}NO)_2(\mu\text{-}O_2CR)_4(ArH)_2]$ (ArH = benzene or toluene) in which arene and nitrosyl ligands are coordinated to the terminal palladium atoms [124]. These complexes have also been obtained conveniently by treatment of $[Pd(O_2CR)_2]_3$ with NO in aromatic solvents [124].

Reactions of bulky phosphines and nitrogen containing organic molecules with palladium compounds yield metalated binuclear complexes. However, in certain cases trinuclear complexes are formed. Thus when $PdCl_2$ is treated with TRIP (**13**) in refluxing ethanol-thf mixture, a trinuclear chloro-bridged complex, **14** has been isolated [125]. The central palladium atom in **14** lies at the crystallographic inversion center. The Pd–Cl distances *trans* to phosphorus are longer than the other Pd–Cl distances, as is expected due to strong *trans* influence of the phosphine ligand [125]. Similarly, reactions of palladium acetate with nitrogen containing ligands (*e.g.*, 2-dimethylaminotoluene, N,N-dimethylneopentylamine, 1-*tert*-butylpryrazole, 1,2-(2,6-$Pr^i_2C_6H_3N{=}C)_2C_6H_4$, *etc.*) give trinuclear acetato-bridged orthometalated palladium complexes, $[Pd_3(\mu\text{-}OAc)_4(C^{\cap}N)_2]$ [126–134]. These complexes, formed by electrophilic cleavage of C–H bond, have been proposed as reactive precursors in several catalytic reactions [128,129,131,132]. The complex, $[Pd_3(\mu\text{-}OAc)_4(C^{\cap}N)_2]$ ($C^{\cap}N$ = 2,6-$Pr^i_2C_6H_3N{=}CHC_6H_3CH{=}NC_6H_3Pr^i_2$-2,6), is an active pre-catalyst in Heck coupling reaction of both activated and deactivated aryl bromides [131]. These complexes are formed usually as a mixture of *syn* and *anti* isomers. The molecular structures revealed an 'S'-shaped arrangement (**15**) for "$Pd_3(OAc)_4$" core with a Pd···Pd separation of ~2.95 Å [128–131].

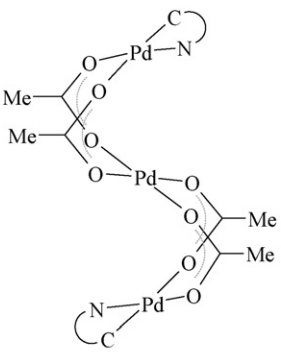


(TRIP)

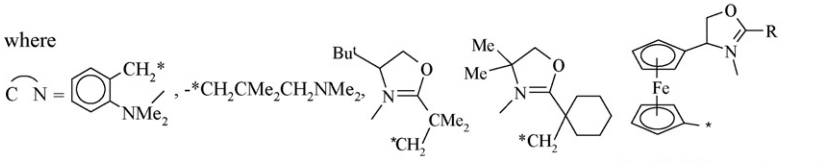
(13)



(14)



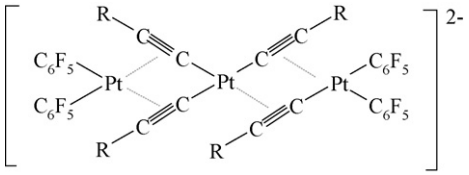
(15) ('S' - Shaped structure)



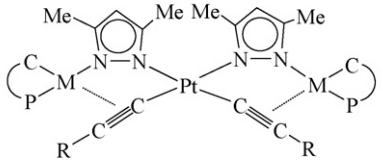
R = Bu^t, Ph, γ-admantyl

* indicates metallation sites

Acetylide-bridged trinuclear complexes have been synthesized using labile $[Pt(C_6F_5)_2(thf)_2]$ [135–138]. Treatment of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ with $[Bu_4N]_2[Pt(C{\equiv}CR)_4]{\cdot}nH_2O$ in diethylether affords doubly acetylide-bridged trinuclear complexes, $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}RC{\equiv}C)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R = Ph, Bu^t, $SiMe_3$) (**16** [135]. The whole anion is not planar. One of the terminal platinum atoms is coordinated to two C_6F_5 groups one σ-bond to acetylene and π bond to C≡C, while the other terminal platinum atom is coordinated with two C_6F_5 groups and 2 π bonds of C≡C-ligand [138]. Reaction of $[Pt_2(C{\equiv}CR)_4(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$ with $[Pt(C_6F_5)_2(thf)_2]$ in 1:1 ratio yield $[Pt_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2(C{\equiv}CR)_2(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$ (R = Bu^t, Ph) [137]. Reaction of $[Pt(C{\equiv}CPh)_2((dmpzH)_2]$ with $[M_2(\mu\text{-}OAc)_2(C{\cap}P)_2]$ ($C{\cap}P = CH_2C_6H_4P(o\text{-}tol)_2$) yields acetylide/pyrozolato-bridged complexes (**17**) [138].



(16)



M = Pd or Pt

(17)

The reaction of acetylplatinum complex, *trans*-$[Pt(COMe)Cl(PPh_3)_2]$ with an excess of dibenzyldisufide in refluxing chloroform yields a trinuclear cationic complex $[Pt_3(\mu\text{-}S)(\mu\text{-}SBz)_3(PPh_3)_3]Cl$, representing the structural motif **XVI** [139]. The structure comprises of planar Pt_3S_3 skeleton capped by the sulfido ligand (Fig. 10). The PPh_3 ligands lie below the Pt_3S_3 plane while the benzyl groups of SBz ligands are arranged above this plane. Reaction of $PdCl_2(PPh_3)_2$ with $PhSe^-$ in 2:1 ratio yields, in addition to dinuclear complex, a trinuclear complex $[Pd_3(\mu\text{-}Se)$

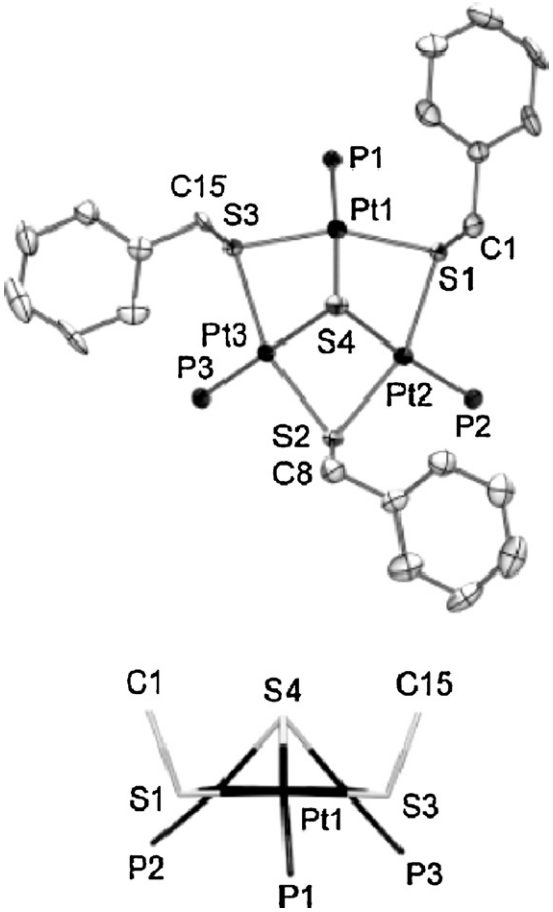
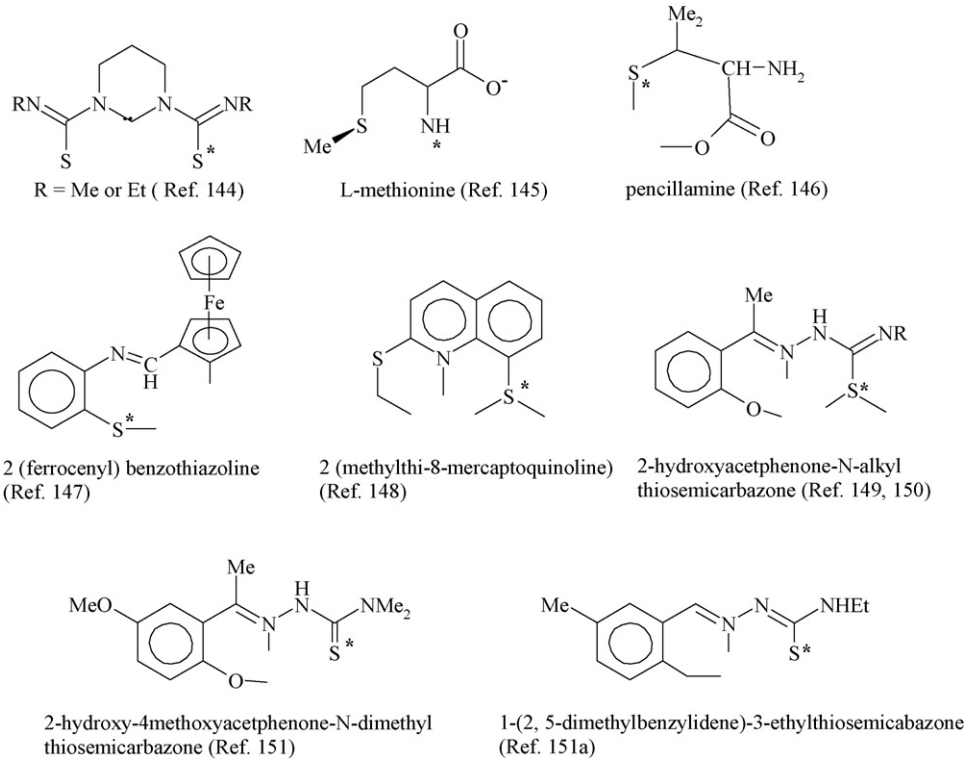
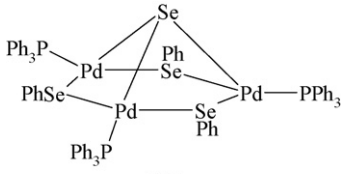


Fig. 10. Structure of $[Pt_3(\mu\text{-}S)(\mu\text{-}SBz)_3(PPh_3)_3]Cl$; [139] (Reproduced with the permission of American Chemical Society).



Scheme 8.

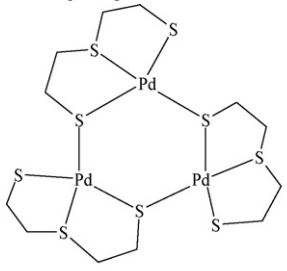
$(\mu\text{-SePh})_3(PPh_3)_3]Cl$ [140]. Each palladium atom is bridged through phenylselenolate to two other palladium atoms while the selenide ligand caps all the three-palladium atoms (**18**) [140].



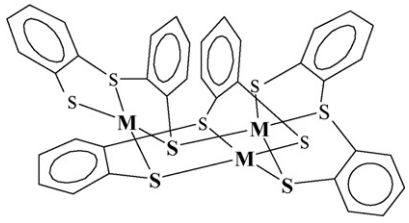
(18)

2.2.3. Triangular complexes

Trinuclear complexes in a triangular arrangement having different conformations, *viz.* chair, twist-boat, crown or basin shaped, have been isolated primarily using thiolate ligands. The reaction of 2, 2′-dimercaptodiethylsulfide ($(HSCH_2CH_2)_2S$) with K_2PdCl_4 in water acetone yields orange crystals of a trinuclear complex, $[\{Pd(SCH_2CH_2)_2S\}_3]$ (**19**) [141]. Each palladium is surrounded by four sulfur ligands, one of the thiolate of each ligand is shared by two-palladium atoms forming a six-membered ring of alternating palladium and sulfur atoms. The bridging sulfur atoms lie at the corner of a triangle. The three-palladium square planes are inclined towards each other so that molecule adopts a basin shaped conformation [141]. Similarly palladium and platinum complexes with bis(2-mercaptophenyl)sulfide have been synthesized [142,143]. The six-membered M_3S_3 (M = Pd or Pt) ring (**20**) adopts a chair conformation that leads to a propeller-like twist of three "$M(S_3)$" fragments. Several trinuclear complexes, showing similar chair conformations of the six-membered ring, have been synthesized with a variety of tridentate ligands (Scheme 8) [144–151a]. The six-membered Pd_3S_3 ring in $[Pd_3(\mu\text{-SEt})_3(S_2CSEt)_3]$ also adopts a chair conformation [152]. The bridging SEt ligands are disposed in a *syn–endo* fashion [152].



(19)



(20)

Several complexes of composition $[M_3X_3L_3]$ (**21**) (M = Pd or Pt; X = Cl or Br; L = bidentate ligand) have been prepared by the reaction of MCl_4^{2-} with internally functionalized organochalcogenolate ligands, *viz.* $Me_2NCH_2CH_2E$ (E = S [153], Se [154]) and 2-mercapto nicotinic acid [155]. Chalcogenolate and nitrogen atom form a chelate and the former bridges two metal atoms so as to give a six-

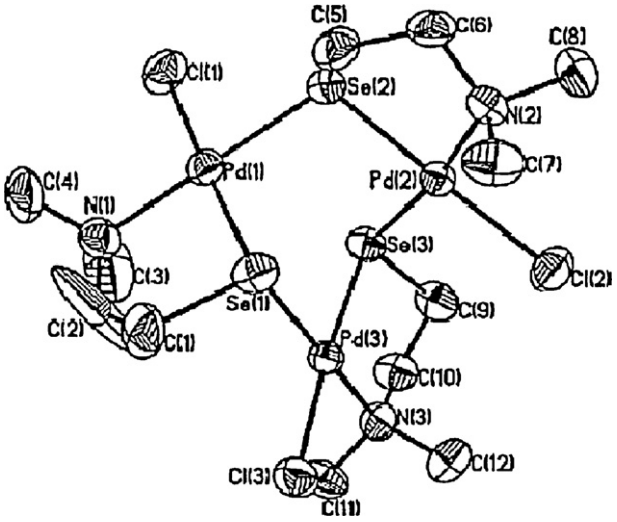
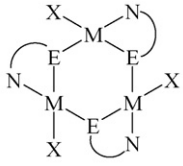


Fig. 11. Molecular structure of $[Pd_3Cl_3(SeCH_2CH_2NMe_2)_3]$; [154] (Reproduced by permission of the Royal Society of Chemistry).

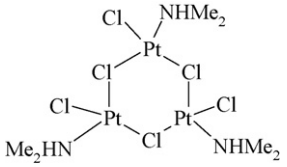
membered ring which acquires a twist-boat conformation (Fig. 11) [153–157].



M = Pd or Pt; X = Cl or Br; E = S or Se

(21)

Complexes with triangular motifs stabilized with other bridging ligands such as OH [158–165], halide [166] and phosphide [167] have been synthesized. A variety of aquated species have been identified during the course of hydrolysis of $PtCl_2(N,N)$ complexes while investigating their antitumor activity [158–161]. In fact the complex *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ exists in an equilibrium with di- and trimeric species and their relative concentration is pH dependent [158,162]. In the trinuclear complexes the three planar *cis*-$[Pt(OH)_2(N,N)]$ fragments share OH corners giving rise a Pt_3O_3 ring which assumes a chair conformation [161]. Dichloromethane solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(NHMe_2)_2]$ on standing yields red crystals of a chloro-bridged trimer $[PtCl_2(NHMe_2)]_3$ (**22**) [166]. The six-membered Pt_3Cl_3 ring assumes a "crown" conformation with C_3 symmetry. All the bridging chlorides lie on the same side of the Pt_3 plane. The terminal Pt–Cl distance (2.274 (3) Å) is shorter than the bridging Pt–Cl distances (2.332 (3) and 2.319 (3) Å (Table 4) [166]. Reaction of $[PdCl_2COD]$ with PH_2CH_2Fc in the presence of PPh_3 yields an orange colored trinuclear complex, $[Pd_3(\mu\text{-}PHCH_2Fc)_3Cl_3(PPh_3)_3]$ [167].



(22)

Dialkylsulfide-bridged organoplatinum complexes, $[Pt_2R_4(SR'_2)_2]$ (R = Me, Ph or tol; R′ = Me, Et, Pr^n, Pr^i) are important synthons for the preparation of a wide variety of organoplatinum complexes and exist as R'_2S bridged dimeric complexes. However, in case of $[PtPh_2(SMe_2)]_n$ (n = 2 or 3) trimeric form predominates (90%) over dimeric form as shown by X-ray crystallography. The complex has three bridging dimethylsulfide ligands with

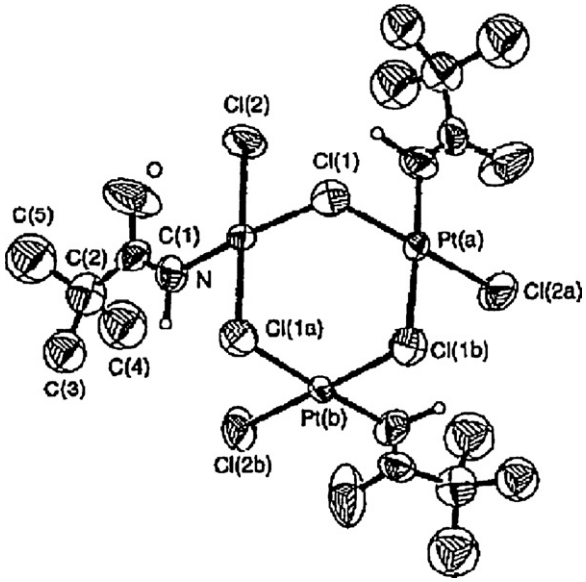


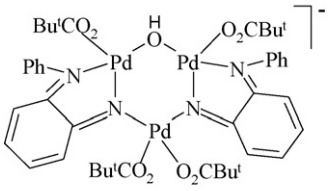
Fig. 12. Molecular structure of $[PtCl_2(HN{=}C(OH)Bu^t)]_3$; [170] (Reproduced by permission of the Royal Society of Chemistry).

the two-phenyl groups on each platinum atom [168]. A similar structure for $[Pt(CH_2SiMe_3)_2(SMe_2)]_3$ has been reported earlier [169]. The formation of trimeric structures in these cases has been attributed to the steric factors—bulky phenyl and trimethylsilylmethyl groups. A similar structure has been observed in case of $[Pd_3(\mu\text{-}SeCH_2CH_2COOEt)_3(\eta^3\text{-allyl})_3]$ [24], whereas with simple chalcogenolato ligand $[Pd_2(\mu\text{-}ER)_2(\eta^3\text{-allyl})_2]$, dimeric structure exists both in solution and in the solid state.

Disproportionation of $[PtCl_2\{HN{=}C(OH)Bu^t)_2]_2$ in dichloromethane yields an orange hexagonal prismatic crystals of $[PtCl_2\{HN{=}C(OH)Bu^t\}]_3$ in which three platinum square planes are mutually orthogonal (structure form **XV**) (Fig. 12). The structure is one half of the cubic β-$[PtCl_2]_6$ with the vacant site occupied by the emine ligands [170].

The reaction of $PdCl_4^{2-}$ with [21] aneN_7 in aqueous medium affords a trinuclear complex, $[Pd_3([21]aneN_7)Cl_3][ClO_4]_2{\cdot}H_2O$ formed by acidic dissociation of an amino group of the mecrocylic ligand [171]. In the complex, the two-palladium square planes are parallel while third plane forms an angle of 92.0° with the former two planes [171]. The reaction of lithium salt of 2,5-bis{2-(4,4′-dimethyl-4,5-dihydroxazolyl)}pyrole (dmoxpH) with $PdCl_2$(COD) primarily yields a binuclear orange complex, $[Pd_2Cl_2(dmoxp)_2]$ together with a minor yellow trinuclear complex, $[Pd_3Cl_4(dmoxp)_2]$ in which three-palladium square planes are mutually orthogonal [172]. The complex on attempted recrystallization yields binuclear complex and $PdCl_2$ [172].

The reaction of $Pd(CN)_2$(dppe) with $AgClO_4$ in acetonitrile affords a trinuclear cyano-bridged complex, $[Pd_3(CN)_3(dppe)_3][ClO_4]_3$. All the three-cyano bridges lie on one side of the Pd_3 plane [173]. Treatment of $[Pd(O_2CBu^t)_2]_3$ with N-phenyl-*o*-phenylene diamine in the presence of KOH in *m*-xylene gave an anionic trinuclear complex $K[Pd_3(O_2CBu^t)_4(\mu\text{-}OH)\{\mu\text{-}N,N\text{-}\eta^2\text{-}N,N\text{-}(N)(NPh)(C_6H_4)\}_2]$ (**23**) which has both hydroxo and imine bridges [174].



(23)

Table 4
Triangular complexes of palladium(II) and platinum(II) characterized by X-ray crystallography.

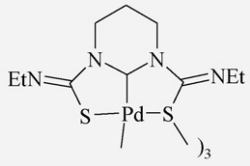
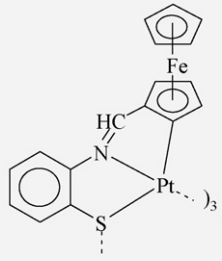
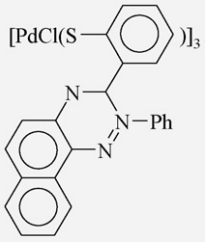
Complex	Comment	Reference
$[Pd\{SCH_2CH_2)_2S\}]_3$	Pd···Pd = 3.407 (12)–3.662 (12) Å Pd–S = 2.234 (34)–2.409 (32) Å Pd-planes are inclined towards each other so as to give basin shaped structure	[141]
$[Pd_3(\mu\text{-}SEt)_3(S_2CSEt)_3]$	Pd···Pd = 3.303 (2)–3.655 (2) Å Pd–S = 2.318 (5)–2.349 (5) Å Six-membered Pd_3S_3 ring adopts a chair conformation	[144]
$[Pd_3\{(S\text{–}C_6H_4)_2S\}_3]$	Pd···Pd = 3.409 (4)–3.553 (4) Å Pd–S = 2.257 (7)–2.343 (7) Å	[143]
$[Pt_3\{(SC_6H_4)_2S\}_3]$	Pt···Pt = 3.386 (1)–3.620 (1) Å Pt–S = 2.251 (3)–2.327 (3) Å Pt_3S_3 in chair conformation	[142]
$[Pd_3Cl_3(\text{mercaptonicotinic acid})_3]$	Pd···Pd = 3.55 Å, Pd–S = 2.305 (2) Å Pd–N = 2.043 (5) Å; Pd–Cl = 2.330 (2) Å Pd_3S_3 in chair conformation	[145]
$[Pt_3Br_3(SCH_2CH_2NMe_2)_3]$	Pt–S = 2.255 (4)–2.305 (4) Å Pt–Br = 2.439 (3)–2.470 (2) Å Pt_3S_3 ring twist-boat conformation	[146]
$[Pd_3Cl_3(SeCH_2CH_2NMe_2)_3]$	Pd–Se = 2.367–2.419 Å Pd–Cl = 2.356 (av) Å Pd–N = 2.136 (av) Å Pd_3S_3 twist-boat conformation	[147]
$[Pt_3Cl_3\{SCH_2CH(COOH)NH_2\}_3]$		[157]
	Pd_3S_3 adopts a chair conformation	[148]
$[Pt_3(OOC\text{–}CH(NH)CH_2CH_2SMe]_3]$	Pt–O = 2.03 (1) (av) Å Pt–N = 1.98 (1)–2.11 (3) Å Amido-bridged trimer with a chair shaped $(Pt\text{–}N)_3$ ring	[149]
$[Pd\{SC(Me_2)CH(COO)NH_2\}]_3$	Pd···Pd = 3.017 (2)–3.226 (1) Å Pd–N = 2.08 (av) Å Pd–O = 2.07 (av) Å	[150]
	Pt···Pt = 3.535 (9)–3.698 (9) Å Pt–S = 2.27 (5)–2.37 (4) Å	[151]
$[Pd\{2\text{-}CH_2\text{-}5\text{-}MeC_6H_5C(H)=NN=C(S)NHEt\}]_3$	six-membered symmetrical Pd_3S_3 core Pd–C = 2.038 (11) Pd–N = 2.001 (11) Pd–S = 2.403 (3), 2.322 (4) Å	[151a]
$[Pd(OC_6H_4CMe=N\text{–}NH\text{–}C(S)=NPr)]_3$	Pd···Pd = 3.404 (2)–4.171 (3) Å Pd–N = 2.009 (3)–2.015 (3) Å Pd–O = 1.970 (4)–1.996 (3) Å Pd–S = 2.2251 (18)–2.3386 (1) Å	[153]
$[Pd(OC_6H_4CMe=N\text{–}NH\text{–}C(S)=NEt)]_3$	Pd···Pd = 3.500 (1)–4.146 Å	[154]
$[Pd(OC_6H_4CMe=N\text{–}N=C(S)\text{-}NMe_2)]_3$	Pd···Pd = 3.4118 (5)–3.6528 (3) Å Pd–S = 2.2536 (13)–2.3579 (12) Å Pd_3S_3 in chair conformation	[155]

Table 4 (*Continued*)

Complex	Comment	Reference
	Pd···Pd = 3.4812 (8)–3.7627 (8) Å Pd_3S_3 ring adopts a twist-boat conformation	[156]
$[Pt(OH)(NH_3)_2]_3[SO_4]_3{\cdot}6H_2O$		[158]
$[Pt(OH)(NH_3)_2]_3[NO_3]_6{\cdot}6H_2O$		[159]
$[Pt(OH)(trans\text{-}1,2\text{-diaminocyclohexane})]_3[SO_3]_3{\cdot}14H_2O$	Pt···N = 2.021 (av) Å Pt–O = 2.034 (av) Å Pt_3O_3 chair conformation	[161]
$[Pt_3(\mu\text{-}OH)_3(COD)_2(Bian)[OTf]_3$ (Bian = bis(3,5-diisopropylphenylimino)acenaphthene)	Pt–O = 2.001 (6)–2.080 (6) Å O–Pt–O = 88.3 (2), 90.0 (2), 92.4 (2)°	[165]
$[Pt_3(\mu\text{-}PHCH_2Fc)_3Cl_3(PPh_3)_3]$	Pd–Cl = 2.3735 (15)–2.4120 (16) Å	[167]
$[PtCl_2(NHMe_2)]_3$	Pt–N = 2.046 (9) Å Pt–Cl–2.274 (3)–2.332 (3) Å Pt_3Cl_3 assumes a crown conformation	[166]
$[PtCl_2(HN{=}C(OH)Bu^t)]_3$	Pt···Pt = 3.527 (1) Å Pt–N = 2.003 (15) Å Pt–Cl = 2.315 (5), 2.340 (4) Å Pt planes mutually orthogonal	[170]
$[PtPh_2(SMe_2)]_3$	Pt···Pt = 4.052 (1) Å Pt–S = 2.385 (2) Å Pt–C = 2.003 (9) Å	[168]
$[Pd_3(\mu\text{-}SeCH_2CH_2COOEt)_3(\eta^3\text{-}allyl)_3]$	Pd–Se = 2.463 (av) Å Se–Pd–Se = 92.01, 89.20, 90.88°	***[24]
$[Pd_3([21]aneN_7)Cl_3][ClO_4]_2{\cdot}H_2O$	Pd···Pd = 3.057 (4)–3.478 (4) Å	[171]
$[Pd_3Cl_4(dmoxp)_2]$	Pd–Cl = 2.275 (2)–2.283 (1) Å Pd–N = 2.011 (3)–2.010 (4) Å	[172]
$[Pd_3(CN)_3(dppe)_3][ClO_4]_3$	Pd–C = 2.02 (1) Å Pd–N = 2.07 (1) Å	[173]
$[K{\cdot}H_2O][Pd_3(O_2(Bu^t)_4(\mu\text{-}OH)\{\mu\text{-}N, N\text{-}\eta^2\text{-}N, N'\text{-}N(NPh)(C_6H_4)\}_2]$	Pd···Pd = 3.330 (1)–3.459 (1) Å Pd–N = 1.964 (7)–2.001 (7) Å Pd–O = 2.009 (6)–2.025 (6) Å	[174]

2.3. Trinuclear carboxylato/pyrazolato-bridged complexes

Palladium acetate is an important reagent widely used in several organic syntheses and for the preparation of palladium based catalysts, and of late in materials science for the preparation of thin films [175,176], nanoparticles [177–180] and nanowires [181] of palladium. The acetate and other palladium carboxylates were first synthesized by Wilkinson and co-workers [182]. The palladium acetate is usually prepared by dissolving activated palladium metal in refluxing glacial acetic acid in the presence of deficient amount of concentrated nitric acid [182,183]. To avoid the formation of any nitrogen oxide containing product, it is essential to have some undissolved metal at the end of the reaction [182] and also an inert gas (*e.g.*, N_2) to be bubbled through the boiling reaction mixture to displace brown fumes of NO_2 (Eq. (20)) [183]. Palladium acetate can also be prepared from palladium metal in acetic acid at 100 °C in the presence of oxygen [184]. Other palladium carboxylates are prepared by acetate exchange reactions between palladium acetate and an appropriate carboxylic acid (Eq. (21)) [182,185–187], although propionate could be isolated in a manner similar to acetate [182]:

$$3Pd + 6AcOH + 6HNO_3 \rightarrow [Pd(OAc)_2]_3 + 6H_2O + 6NO_2 \quad (20)$$

$$[Pd(OAc)_2]_3 + 6RCOOH \rightarrow [Pd(O_2CR)_2]_n + 6AcOH$$
$$(R = Et,\ Bu^t,\ Bu^i,\ CF_3,\ C_2F_5,\ Ph,\ 2,4,6\text{-}Me_3C_6H_2;$$
$$C(R) = CHMe\ (R = H\ or\ Me) \quad (21)$$

Osmometric molecular weight determination of palladium acetate and propionate in benzene at 37 °C supports a trimeric structure but in refluxing benzene monomeric form persists [182]. Subsequent studies on nuclearity of palladium acetate in solution (trinuclear [189] or a mixture of various aggregates [190]), however, remains inconclusive. Palladium benzoate, on the other hand, retains its trimeric structure in solution in the temperature range 37–132 °C [182].

^{1}H NMR spectrum of palladium acetate is of interest. The spectrum in rigorously dried $CDCl_3$ exhibits a singlet due to AcO group at δ 2.01 ppm, but in solvents containing traces of moisture displays five peaks at around 2 ppm [183]. This has been attributed to hydrolysis of one of the acetate ligands leading to break down of the D_{3h} symmetry, consequently making acetate groups non-equivalent [191]. The absorption spectrum of palladium acetate in benzene exhibits a band at λ_{max} 399 nm attributable to $d_{\sigma^*}p_{\sigma}$ transition in the Pd_3 core [191]. The compound is emissive in benzene solution at room temperature [191]. The emission spectrum shows

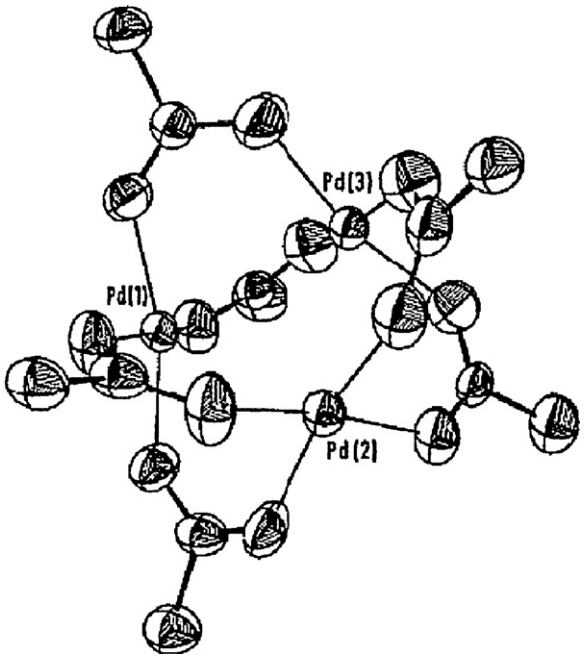


Fig. 13. Molecular structure of $[Pd(OAc)_2]_3$; [192] (Reproduced by permission of the Royal Society of Chemistry).

a band at 475 and a weaker emission at 595 nm, which originate from d_{σ^*}–p_σ excited state of Pd_3 core [191].

Homoleptic palladium carboxylates, $[Pd(O_2CR)_2]_3$ (R = Me, Et, Bu^i, Bu^t, CF_3, CMe=HMe, 2,4,6-$Me_3C_6H_2$), have been structurally characterized (Table 5) [185–188,192–196]. All of them are composed of Pd_3 triangles in an approximate D_{3h} symmetry. The Pd_3 core varies from equilateral to isosceles planar triangular arrangement. The formation of isosceles triangles in several cases has been attributed to intermolecular packing forces [185]. Each square-planar palladium atom is held together by a pair of carboxylate bridges, one above and another below the Pd_3 plane, (Fig. 13).

Since palladium acetate is often associated with solvent molecules like H_2O, C_6H_6, CH_2Cl_2, its physical properties (*e.g.*, m.p., 205 and 235 °C [196]) and chemical reactivates varies markedly [196,197]. The palladium–oxygen bonds are rather labile, so that several reactions of palladium acetate are observed. Palladium carboxylates react with various neutral N, P, As donor ligands to give mononuclear complexes, $[Pd(O_2CR)_2(L_2)]$, in which carboxylate functions as monodentate ligands [182,198]. Several substitutions reactions in which acetate ligands are partially or completely replaced by incoming anionic ligands have been observed. One of the acetate ligands is readily replaced by a stronger bidentate ligand to yield $[Pd_3(OAc)_5L]$ which are kinetically less labile than the acetate, $[Pd(OAc)_2]_3$, itself. The complexes, $[Pd_3(OAc)_5(NO_2)]$ [183,199] and $[Pd_3(OAc)_5(oxazolone)]$ [200], for instance, preserve the Pd_3 core of $[Pd(OAc)_2]_3$ with the exception that one of the acetate group is replaced by bidentate L (NO_2^- or oxazolone). The ^1H NMR spectra of these complexes show five acetate resonances of equal intensity [183,200].

The reactions of palladium carboxylates with a variety of α-substituted thioether, R′SCH(R″)Z (Z = ester, ketone, sulfone, substituted methyl), [201–206] and oximes [207,208] result into the formation of trisubstituted products, $[Pd_3(O_2CR)_3(L_3)]$ (Eqs. (22) and (23)). These complexes are formed by replacement of three acetate ligands on one side of the Pd_3 plane of $[Pd(O_2CR)_2]_3$ by three bidentate ligands bonded in a η^2-fashion [201,207,208]. Each square-planar palladium atom is bridged by an acetate group and bidentate ligand (methine carbon and sulfur in case of α-substituted thioether, and nitrogen and oxygen in the case of oximes). Complete substitution of acetate groups takes place when $[Pd(OAc)_2]_3$ is treated with acetylacetone, salicylaldehyde or $HSCH_2C(O)Me$ yielding complexes of composition PdL_2 [182,202]:

$$[Pd(OAc)_2]_3+3HONC{=}RR' \rightarrow [Pd_3(\mu\text{-}OAc)_3(\mu\text{-}ON\text{-}CRR')_3]+3AcOH,$$
$$R/R' = Me/Me;\ Pr^i/Ph \quad (22)$$

$$[Pd(O_2CR)_2]_3 + R'SCHR''Z \rightarrow [Pd_3(\mu\text{-}O_2CR)_3(\mu\text{-}R'SCR''Z)_3] + 3RCO_2H$$
$$R = Me \text{ or } Ph;\ R' = Me,\ Et \text{ or } Bu^t;\ R'' = H \text{ or } Me;\ Z = COOMe,\ COOEt, \text{ or } C(O)Me \quad (23)$$

The reaction of $[Pd(OAc)_2]_3$ with (R)-para-tolylsulfinyl-2-propanone yields a trinuclear complex, $[Pd(O{=}C(Me)C\text{–}S(O)C_6H_3\text{–}Me]_3$ which is comprised of a nine membered ring of alternating S, Pd, and C(H) atoms [209]. Orthometalation of the ligand is highly seteroselective as the compound is formed in a *RR* configuration with very high specific rotation ($[\alpha]_D^{20} = -486.5$; *C* = 0.2 in $CHCl_3$) [209].

Trinuclear platinum complexes of the types, $[Pt_3(\mu\text{-}OAc)_4(oxmH_2)]$ ($oxmH_2$ = dimethylglyoxime ($dmgH_2$); cyclohexanedioneoxime ($cdoH_2$), dipheylglyoxime ($dpgH_2$) and benzoquinone dioxime ($bqdH_2$)) and $[Pt_3(OAc)_4(N^{\cap}N)_3]^{2+}$ ($N^{\cap}N = NH_2CH_2CH_2NH_2$ or $MeHNCH_2CH_2NHMe$) are formed by cluster core transformation of $[Pt(OAc)_2]_4$ [210,211]. The three platinum atoms form an isosceles triangle with Pt···Pt separation of 2.51–2.61 Å. The platinum atoms at the long edge are each bonded to unidentate acetate while the remaining two acetates groups are bridged to the platinum atoms of two equidistance edges of the triangle [210,211]. The dioxime or en ligands occupy coordination sites of the Pt_3 plane in a chelating fashion.

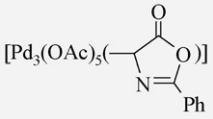
Other ligands, like oxime [212] and pyrazoles [213–215] have been employed to prepare structural analogs of $[Pd(OAc)_2]_3$. The reaction of Li_2PdCl_4 with Z-form of $PhPr^iC{=}NOH$ in the presence of sodium acetate leads to the formation of a trinuclear complex, $[Pd(ON{=}CPr^iPh)_2]_3$ [212], however the E form of the oxime undergoes orthopalladation [216] similar to other oximes containing sterically demanding R groups.

When an acetonitrile solution of $[PtCl_2(pzH)_2]$ is refluxed in the presence of a base (Et_3N), a trinuclear pyrazolato-bridged complex, $[Pt(pz)_2]_3$ is isolated as a colorless crystalline solid in 12% yield [215]. This complex was originally synthesized by heating $[Pt(pz)_2(pzH)_2]_2$ in mesitylene at 185 °C in a sealed tube [213]. The pyrazolato-bridged palladium complexes, $[Pd(Xpz)_2]_3$ (Xpz = pz, 4-Mepz, 3-Phpz) have been synthesized by a reaction between $[PdCl_2(XpzH)_2]$ and a base usually triethylamine [214,215]. The trinuclear pyrazolato-bridged complexes are isomorphous and are comprised of isosceles M_3 triangles in which each metal atom is connected to one another by a pair of pyrozolate bridges (Fig. 14) [213–215]. Oxidation of $[Pt(pz)_2]_3$ by ceric ammonium nitrate in the presence of KBr in CH_2Cl_2/H_2O yields a deep blue mixed valent $Pt^{II,III,III}$ complex $[Pt_3Br_2(pz)_6]$ which has a localized Pt–Pt bond (2.7787 (8) Å) [217].

3. Tetranuclear complexes

Four square planes of palladium and platinum can be assembled through bridging ligands in several ways. Some of the idealized configurations are illustrated in Scheme 9 (**XVII**–**XXIV**), although distortions from these idealized configurations are not uncommon. For instance, four square planes arranged linearly in **XVIII** can be planar, central part planar with terminal planes tilted, hinged at the central part or zig-zag.

Table 5
Trinuclear palladium and platinum(II) carboxylates/pyrazolates characterized by X-ray analysis.

Compound	Comments	Reference
$[Pd(OAc)_2]_3 \cdot \frac{1}{2}H_2O$	D_{3h} symmetry, Pd···Pd = 3.105 and 3.203 Å Pd–O = 1.973–2.014 Å O–Pd–O(trans) = 163.5–168.9°	[192]
$[Pd(OAc)_2]_3$		[195]
$[Pd(OAc)_2]_3 .CH_2Cl_2$		[194]
$[Pd(OAc)_2]_3 .C_6H_6$		[193]
$[Pd(O_2CEt)_2]_3$	Isosceles Pd_3 triangle, Pd···Pd = 3.135 (1)–3.191 (1) Å Pd–O = 1.995 (7) Å (av.) $O–Pd–O_{(trans)}$, 1.661 (23)°	[185]
$[Pd(O_2CBu^t)_2]_3$	Equilateral Pd_3 triangle, Pd···Pd = 3.132 (1) Å Pd–O = 1.980 (11) Å (av.) $O–Pd–O_{(trans)}$ = 166.9 (3)°	[185]
$[Pd(O_2CBu^i)_2]_3$		[187]
$[Pd(O_2CCF_3)_2]_3$		[186]
$[Pd(O_2CC_6H_2Me_3\text{-}2,4,6)_2]_3$	Isosceles Pd_3 triangles, Pd···Pd = 3.140 (3)–3.137 (3) Å Pd–O = 2.00 (2) Å (av.) $O–Pd–O_{(trans)}$ = 166.6 (46)°	[185]
$[Pd(O_2C–C(Me)=CHMe)_2]_3$	Isosceles Pd_3 triangle Pd···Pd = 3.0930–3.1707 Å	[188]
$[Pd_3(OAc)_5(NO_2)]$	Pd···Pd = 3.085 (1)–3.121 (1) Å Pd–O = 2.00 (1) Å Pd–N = 1.97 (1) Å	[185,199]
	Pd–O = 1.995 (3)–2.086 (3) Å Pd–N = 2.003 (3) Å	[200]
$[Pd_3(OAc)_3(MeSCHCOOEt)_3]$	Pd···Pd = 3.170 (2)–3.2434 (9) Å Pd–S = 2.268 (av) Å Pd–O = 2.055 (3)–2.129 (2) Å Pd–C = 2.043 (av) Å	[201]
$[Pd_3(OAc)_3(ON=CMe_2)_3]$	Pd···Pd = 2.998 (4)–3.019 (4) Å Pd–O = 1.98 (3)–2.08 (3) Å Pd–N = 1.97 Å	[207]
$[Pd_3(OAc)_3(ON=CPr^iPh)_3]$	Pd···Pd = 3.0146 (15)–3.0712 (17) Å Pd–O = 1.996 (8)–2.021 (8) Å Pd–N = 2.002 (10) Å	[208]
$[Pt_3(OAc)_4(cdoH)_2(cdoH_2)]$	Pt···Pt = 2.542 (1)–2.605 (1) Å Pt–O = 2.02 Å (av.) Pt–N = 2.15 (av) Å	[210,211]
$[Pt_3(OAc)_4(dmgH)_2(dmgH_2)]$	Pt···Pt = 2.516 (1)–2.605 (1) Å Pt–O = 2.01 (av) Å Pt–N = 2.13 (av) Å	[211]
$[Pt_3(OAc)_4(Me_2en)_3][ClO_4]_2$	Pt···Pt = 2.564 (2), 2.592 (2) Å Pt–O = 1.99 (av) Å Pt–N = 2.20 (av) Å	[211]
$[Pd(ON=CPr^iPh)_2]_3$	Pd···Pd = 2.887–2.901 (3) Å Pd–O = 2.00–2.03 (2) Å Pd–N = 1.99–2.03 (2) Å	[212]
$[Pt(pz)_2]_3$	Pt···Pt = 3.034–3.067 Å Pt –N = 1.996 (5)–2.027 (5) Å	[213]
$[Pd(pz)_2]_3$	Pd···Pd = 3.0270 (4)–3.0607 (4) Å Pd–N = 1.985 (3)–2.026 (3) Å	[215]
$[Pd(4\text{-}Mepz)_2]_3$	Pd···Pd = 3.0433 (4)–3.0727 (4) Å Pd–N = 1.999 (3)–2.029 (3) Å	[215]
$[Pd(3\text{-}Phpz)_2]_3$	Pd···Pd = 2.997 (1)–3.087 (1) Å Pd–N = 1.963 (9)–2.027 (8) Å	[214]

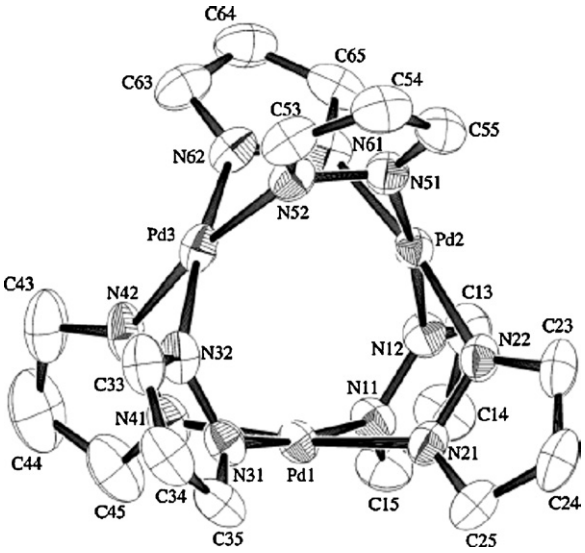


Fig. 14. Molecular structure of $[Pd(\mu\text{-}pz)_2]_3$; [215](Reproduced by permission of American Chemical Society).

3.1. Tetranuclear complexes without metalated ligands

Reactions of *cis*-$[M(C_6R_5)_2(thf)_2]$ with $M'X_2(COD)$ yields complexes of compositions $[(C_6R_5)_2M(\mu\text{-}X)_2M'(COD)]_n$ (R = F or Cl; M and M′ = Pd or Pt; X = Cl, Br, I) which exist as a binuclear species ($n = 1$) in $CHCl_3$ solution, but in the solid state tetranuclear ($n = 2$) species is formed as revealed by the structural analysis of $[\{(C_6F_5)Pt(\mu\text{-}Br)(\mu\text{-}Br)\}_2\{Pd(COD)\}_2]$ [217a]. The two "$Pt(C_6F_5)_2$" and "Pd(COD)" fragments are connected in an alternative way through bromide bridges (structural type **XVII**) [217a].

Linearly bridged tetranuclear complexes (structural type **XVIII**) have been isolated with thiolato and phosphido bridging ligands. Tetranuclear thiolato-bridged complexes, $[Bu_4N]_2[(C_6F_5)_2M'(\mu\text{-}SC_6F_5)_2M(\mu\text{-}SC_6F_5)_2M(\mu\text{-}SC_6F_5)_2M'(C_6F_5)_2]$ (M, M′ = Pd or Pt), have been prepared as red solids by the reactions of $[Bu_4N]_2[[M_2(SC_6F_5)_6]$ with *cis*-$[M'(C_6F_5)_2(thf)_2]$ in 1:2 molar ratio in dichloromethane [96]. The X-ray structural analysis of $[Bu_4N]_2[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$ revealed that the central part of the anion is planar with the thiolate groups adopting an *anti* configuration. The 'PdS$_2$Pt' rings are non-planar with the dihedral angle of 28.2° and the bridging thiolates exhibit a *syn–endo* conformation (Fig. 15) [96].

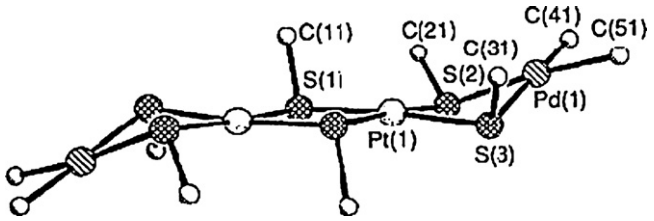
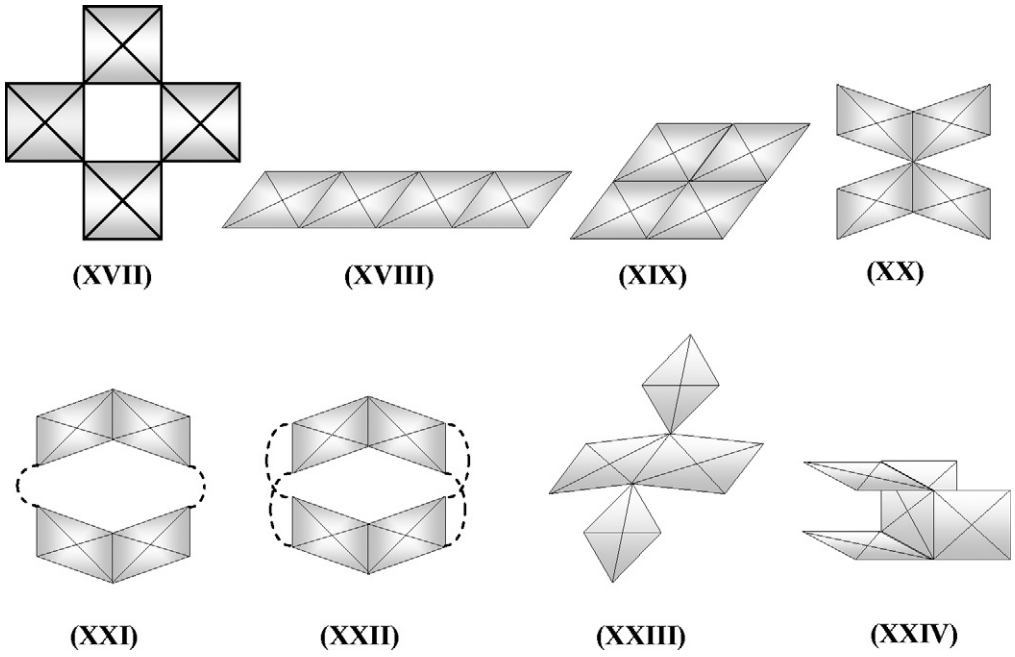
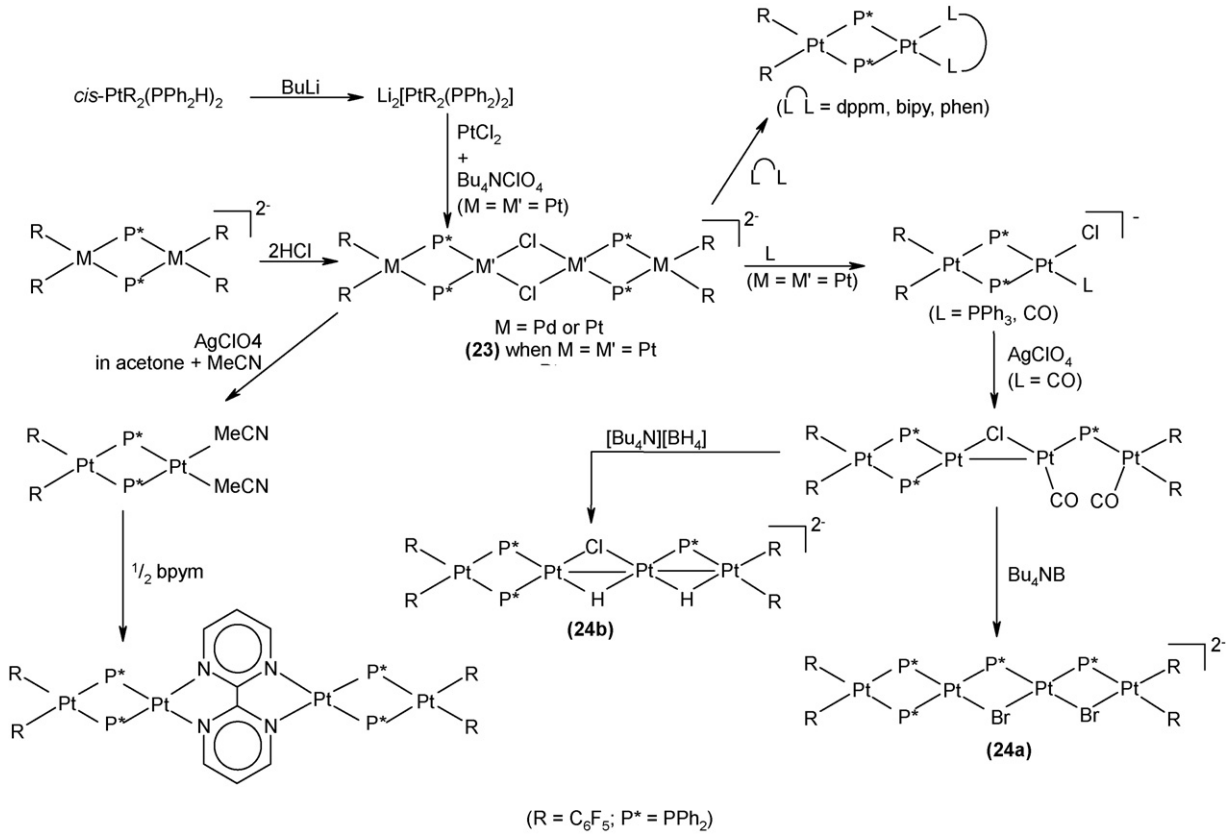


Fig. 15. The skeleton of $[(C_6F_5)_2Pd(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]$; [96] (Reproduced by permission of the Royal Society of Chemistry).

Tetranuclear phosphido-bridged complexes have been isolated by the cleavage of M–C bands in binuclear complexes, $[Bu_4N]_2[C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]$ with an aqueous solution of HCl in 1:2 molar ratio [218]. In an alternative preparation, the complex $Li_2[cis\text{-}Pt(C_6F_5)_2(PPh_2)_2]$ was treated with $PtCl_2$ in the presence of Bu_4NClO_4 in thf [218]. A variety of chemical reactions of these tetranuclear complexes have been studied (Scheme 10) and several of the resulting products have been characterized by X-ray crystallography [79,218–222]. Tetranuclear platinum complexes, $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)]_2$ react with neutral donor ligands like CO, PPh_3, dppm, bipy, phen, to yield binuclear anionic (with CO and PPh_3) and neutral (with bidentate ligands) derivatives [218–220]. Chloride abstraction in $[Bu_4N]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)]_2$ (**23**) by $AgClO_4$ results in to a variety of products depending on reaction conditions [79,221,222]. The reaction in dichloromethane affords a tetranuclear 58-electron cluster, $[Pt_4(\mu\text{-}PPh_2)_3\{\mu\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}k^3\text{-}P\}(C_6F_5)_4]$ containing three Pt–Pt bonds [221], whereas the reaction in acetone–acetonitrile mixture yields a neutral binuclear complex, $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(MeCN)_2]$ [222]. The latter serves as a precursor for the synthesis of a variety of bi-, tri-, tetra- and octa-nuclear homo- and hetero-metallic complexes [222]. The



Scheme 9.



Scheme 10.

chloride abstraction in **23** and related derivatives in the presence of $PtCl_2(PPh_3)_2$ in dichloromethane–acetone mixture results in the formation of neutral trimeric complexes, $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$ (M = Pd or Pt) in which bridging chloride can be substituted with other anionic ligands like OH, Br, SPh, *etc.* [79].

Binuclear phosphido-bridged complex, $[Bu_4N][(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(CO)Cl]$, formed by the bridge cleavage of $[Bu_4N]_2[(C_4F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)]_2$ with CO, on chloride abstraction with $AgClO_4$ in dichloromethane yields yet another tetranuclear complex, $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(CO)_2]$ in which two platinum atoms are bridged by a single phosphido ligand while the remaining two are bridged by two phosphido ligands [220]. The reaction of the latter carbonyl complex with Bu_4NBr or $[Bu_4N][BH_4]$ results in elimination of CO with the formation of dianionic complexes, $[Bu_4N]_2[Pt_4(\mu\text{-}PPh_2)_4(\mu\text{-}X)_2(C_6F_5)_4]$ (**24**) (X = Br (**24a**) or H (**24b**) [223]. The structures of both asymmetric (**24a**) and symmetric bromo-bridged $[Bu_4N]_2[Pt_4(\mu\text{-}PPh_2)_4(\mu\text{-}Br)_2(C_6F_5)_4]$ (Fig. 16) complexes have been established by X-ray crystallography. The Pt···Pt separations vary between 3.197 (1) and 3.682 (1) Å (Table 6) [223]. The two PtP_2Pt rings are almost planar, but the anion is bent at the bridging Br atoms with the dihedral angles between the two Pt planes being 24.8° [223].

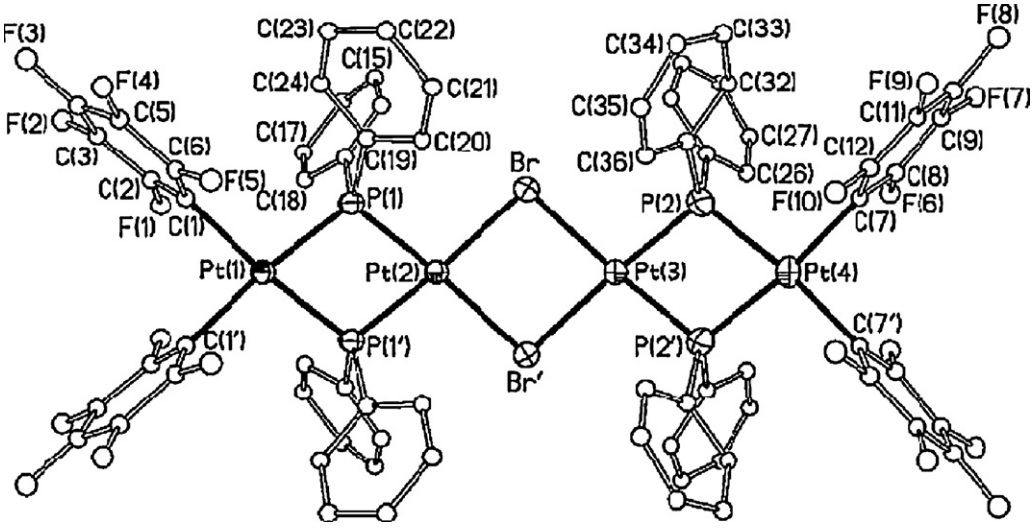
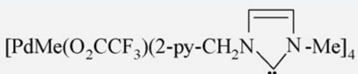


Fig. 16. Molecular structure of $[Pt_4(\mu\text{-}PPh_2)_4(\mu\text{-}Br)_2(C_6F_5)_4]$; [223] (Reproduced with permission of American Chemical Society).

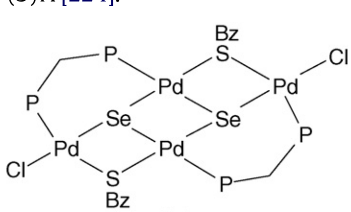
Table 6
Tetranuclear palladium(II) and platinum(II) characterized by X-ray crystallography.

Complex	Comments	Reference
$[\{(C_6F_5)_2Pt(\mu\text{-}Br)(\mu\text{-}Br)\}_2\{Pd(COD)\}_2]$	Eight-membered $Pt_2Br_4Pd_2$ puckered ring Pt–Br = 2.500 (1); 2.524 (1) Å Pd–Br = 2.455 (1), 2.463 (1) Å	[217a]
$[(C_6F_5)_2Pd(SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pt(\mu\text{-}SC_6F_5)_2Pd(C_6F_5)_2]^{2-}$	"PdS_2Pt" non-planar with 28.20° hinge angle "PtS_2Pt" planar	[96]
$[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(CO)_2]$	Phosphido-bridged structure Pt–Pt = 2.6994 (5), 2.6882 (5) Å	[220]
$[Pt_2Pd_2(\mu\text{-}PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)CO]$	M–M[1] = 2.71–2.87 (av) Å	[220]
$[Pt_4(\mu\text{-}PPh_2)_3\{\mu\text{-}PPh(1,2\text{-}\eta^2\text{-}Ph)\text{-}k^3P\}(C_6F_5)_4]$	Pt–Pt = 2.74 (av) Å	[221]
$[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4(bipy)]$	–	[221]
$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}CN)_2Pd(C_6F_5)_2]^{2-}$	Twelve-membered "$Pt_2Pd_2(CN)_4$" ring giving an open cavity	[222]
$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}CN)_2Pt(\mu\text{-}PPh_2)_2\ Pt(C_6F_5)_2]^{2-}$		[222]
$[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Br)\}_2]^{2-}$	Pt–Pt = 3.542 (3)–3.682 (1) Å	[223]
$[Pt_4(\mu\text{-}PPh_2)_4Pt(\mu\text{-}Br)_2(C_6F_5)_4]^{2-}$		[223]
$[Pd_4(\mu\text{-}Se)_2(\mu\text{-}SBz)_2(\mu\text{-}dppm)_2Cl_2]$	Zig-zag chain of palladium square planes with Pd···Pd = 3.191 (3) Å	[224]
$[(Ph_2P)_2NH][Pd_4(\mu\text{-}Cl)_5\{2,4,6\text{-}(CF_3)_3C_6H_2\}_4]$	μ_4-Cl bridged complex μ_4-Cl–Pd = 2.56 (av) Å	[225]
$[Pd_4(\mu_4\text{-}O)_2(\mu\text{-}Cl)_2(dpm)_4]$	Pd···Pd = 3.069 (1) Å	[226]
$[Pd_4(\mu\text{-}S)(\mu\text{-}OH)_2(C^{\cap}N)_4]$	Pd–S = 2.29 (av) Å Pd–O = 2.11 (av) Å	[227]
$[Pd_4(\mu\text{-}S)(\mu\text{-}Cl)_2(C^{\cap}N)_4]$	Pd–S = 2.3067 (19)–2.3196 (19) Å Pd–Cl = 2.432 (2)–2.466 (2) Å	[227]
$[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}PPh_2)_2(C_6F_5)_4]^{2-}$	"$PdCl_2Pd$" ring non-planar	[228]
$[Pt_4(\mu\text{-}PPh_2)_2(\mu\text{-}I)_2(\mu\text{-}I)_2(C_6F_5)_2(PPh_2C_6F_5)_2]$	Pt–I = 2.5861 (5)–2.7556 (5) Å Pt···Pt = 3.299 Å	[229]
$[Pd_4(\mu\text{-}Cl)_2(\mu\text{-}Me_2PCH_2PMe_2)_2(\mu\text{-}SMe)_4]^{2+}$	Pd···Pd = 3.04(av), 3.17(av) Å	[234]
$[\{Pd_2Br_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)\}_2(\mu\text{-}CN)_2]$	"$Pd_2(dppm)_2(CN)_2$" 14-atom ring adopts a chair conformation	[235]
$[PtCl(C_3H_5)]_4$	Pt·····Pt = 3.270 (2), 3.235 (2) Å	[231]
$[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}tolNNNtol)_4]$	Pd–N = 2.011 (4)–2.038 (4) Å Pd–Pd = 2.75 (av) Å (trianzene bridged), 3.71(av) Å (chloride bridged)	[236]
$[Pd_4(\mu\text{-}NO)_2(\mu\text{-}O_2CBu^t)_6]$	Pd···Pd = 3.00 (av) Å Pd–N = 1.91 (a) Å Pd–O = 2.009 (6)–2.063 (5) Å	[238]
$[Pt_4(\mu\text{-}NO)_2(OAc)_6]$	Pt–Pt = 2.944 (2)–3.300 (2) Å Pt–O = 2.042 (av) Å Pt–N = 1.912 (av) Å	[240]
$[Pd_4(\mu\text{-}SEt)_4(OAc)_4]$	Pd···Pd = 3.036–3.195 Å	[242]
$[Pd(\mu\text{-}SePh)(\mu\text{-}OAc)]_4$	Pd–Se = 2.370 (3)–2.423 (3) Å Pd–O = 2.055 (1)–2.082 (14) Å Pd···Pd = 2.864 (18)–3.496 (2) Å	[243]
$[Pt_4(Spy)_2(C_6F_5)_8]^{2-}$	All the three electron pairs on sulfur are coordinated to platinum atoms	[30]
$[Pt_4\{(\mu_3\text{-}S)(SCOEt)\}_2(C_6F_5)_8]^{2-}$		[245]
$[(COD)_4Pt_4(\mu^3\text{-}O)_2Cl_2]^{2-}$	Pt–O = ~2.01 Å Pt–Pt = 3.0391 (8) Å	[246]
$[Pd_4(\mu\text{-}OAc)_4\{\mu\text{-}C_6H_2(NCH_2Bu^t)_4\}_2]$	Pd–N = 1.97Å Pd–O = 2.051 (5) Å Pd···$Pd_{(OAc)}$ = 2.94 (1) Å	[244]
$[(COD)_4Pt_4(\mu^3\text{-}O)_2(\mu\text{-}OH)]^{3-}$	Pt–O = 2.012 (8)–2.062 (8) Å	[246]
$[Na]_2[Pd_4(\mu\text{-}Cl)_4\{\mu\text{-}CH_2P_2(O)_2(OH)_2\}_2\{\mu\text{-}CH_2P_2(O)(OH)_3\}_2]\cdot 8H_2O$	Pd···Pd = 3.539 (1), 3.332 (1) Å	[248]
$[Pt\{(R,S)Ph(O)PCH_2CH_2P(O)Ph\}]_4$	Pt···Pt = 3.335 (3), 3.852 (2) Å Cyclic tetramer Pt–O = 2.103 (7)–2.146 (7) Å Pt–P = 2.20 (av) Å	[252]
$[Pd_2(\mu\text{-}Cl)(\mu\text{-}OAc)\{\mu\text{-}C(C_6F_5){=}NMe\}_2]_2$	Crown shaped structure Pd–O = 2.021 (6)–2.094 (6) Å	[251]
$[PdBr\{Ph_2P\text{–}C_6H_3O(OH)\}]_4$	Pd···Pd = 3.460 (2)–3.578 (2) Å Pd–O = 2.025 (13)–2.138 (13) Å Molecule has a cubic Pd_4O_4 core	[253]
$[Pt(\mu\text{-uracilate-N1, N3})(en)]_4[NO_3]_4$	Pt–N = 2.028 (14)–2.052 (18) Å cyclic tetramer	[255]

Table 6 (*Continued*)

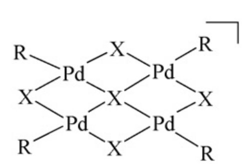
Complex	Comments	Reference
[Pt(μ-pymo)(en)]$_4$[NO$_3$]$_4$	Pt–N = 2.015–2.039 (7) Å N–Pt–N (en) = 83.8 (3)° N–Pt–N (pymo) = 90.1 (3)°	[258]
[Pd(μ-pymo)(en)]$_4$[NO$_3$]$_4$	Pd–N = 2.020–2.033 (2) Å N–Pd–N (en) = 84.25 (9)° N–Pd–N (pymo) = 89.89 (9)°	[258]
[Pd$_4${μ-ON(O)}$_4$(NO$_2$)$_4$(PPr$_3$)$_4$]	Pd–O = 2.14 (1) (av) Å Pd···Pd = 4.886 (2) Å Pd–N = 2.01 (av) Å	[262]
[Pd$_4$(μ-CN)$_4$(C$_6$F$_5$)$_4$(PEt$_3$)$_4$] [Pd(CH$_2$SPh)$_2$]$_4$	Cyano-bridged cyclic tetramer Pd···Pd = 3.304, 4.051 Å	[264] [265]
[Pt(μ-OH)(en)]$_4$[NO$_3$]$_4$	Pt–N = 2.04 (2) (av) Å Pt–O = 2.06 (2) (av) Å	[259]
[Pt$_4$(μ$_4$-CO$_3$)$_2$(NH$_3$)$_8$[NO$_3$]$_4$	Pt–O = 2.03–2.08 Å Pt–O–Pt = 101.1 (5)–105.8 (5) Å	[261]
	Pd–N = 1.99 (2)–2.11 (2) Pd–O = 2.145 (15)–2.170 (15) Å Pd–C (carbene) = 1.89 (3)–1.96 (3) Å Pd–C(methyl) = 1.94 (2)–2.10 (2) Å	[266]
[{Pd(bipy)}$_2${Pd(aet)$_2$}$_2$][NO$_3$]$_4$·5H$_2$O [{Pd(Me$_2$bipy)}$_2${Pd(aet)$_2$}$_2$][NO$_3$]$_4$·3H$_2$O [{Pd(phen)}$_2${Pd(aet)$_2$}$_2$][NO$_3$]$_2$[SiF$_6$]·9H$_2$O [{Pd(phen)}$_2${Pd(aet)$_2$}$_2$][NO$_3$]$_2$[SiF$_6$]$_{1.5}$·11H$_2$O	Pd–S = 2.29, 2.27 (av) Å	[267,268] [268] [268] [268]
[{Pd(SCH$_2$CH$_2$NHCH$_2$CH$_2$CH$_2$NH$_2$)}$_4$] 4[Cl]·4MeOH	Pd···Pd = 3.738 (1), 3.842 (1) Å Pd–S = 2.270 (5), 2.311 (3) Å	[269,270]
[{Pd(SCH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$)$_4$]4[Cl]·Solvents	Pd···Pd = 3.500–3.996 Å Pd–S = 2.267 (5)–2.320 (4) Å	[270]
[{Pd(SCH$_2$CH$_2$NHCH$_2$-py-2)}$_4$][Cl][ClO$_4$]$_3$·Solvent	Pd–Pd = 3.65 (av) Å Pd–S = 2.27, 2.31 (av) Å	[270]
[{Pd(SCH$_2$CH$_2$NHCH$_2$CH$_2$py-2)}$_4$][Cl]$_2$[Pd(SCN)$_4$] [Pd$_4$(TSDO)$_4$]·4H$_2$O·4DMF [Pd(thiosemicarbazone)]$_4$ [Pt(thiosemicarbozone)]$_4$	Pd–Pd = 3.755–3.880 Å Pd···Pd = 3.445–3.850 Å	[270] [272] [273] [273]
[PdCl{SCH$_2$CH(COOH)NH$_2$}]$_4$	Pd···Pd = 3.203 (5), 3.2389 (7) Å Pd–S = 2.2671–2.3000 (9) Å	[275]
[PdI(TeC$_6$H$_4$TeMe-2)]$_4$	Pd···Pd = 3.282 (2), 3.368 (2) Å Pd–Te = 2.513 (2)–2.608 (2) Å "Pd$_4$Te$_4$" ring adopts cradle geometry	[275]
[Pd$_4$(η^3-C$_3$H$_3$)$_4$(μ-bim)$_2$] [Pt(μ-CSe$_3$)(PEt$_3$)]$_4$ [Pd$_4$I$_2$(Spy)$_6$] [Pd$_4$(μ-S$_2$)(3,5-diacetyl-1,2,4-triazole bis(4-ethylthiosemicarbazone)$_2$]	Molecule has a butterfly shape Bridging triselenocarbonate ligand Four-palladium atoms are bridged through disulfide bridge	[278] [279] [252] [274]

Insertion of small molecules across Pd–Pd bond in A-frame palladium(I) complexes [Pd$_2$X$_2$(μ-dppm)$_2$] yields [Pd$_2$(μ-E)(dppm)$_2$X$_2$] (E = S or Se). However, when [Pd$_2$Cl$_2$(dppm)$_2$] is treated with selenium and NaSBz in dmf, a tetranuclear complex, [Pd$_4$(μ-Se)$_2$(μ-SBz)$_2$Cl$_2$(dppm)$_2$] is formed in which four-palladium atoms form a zig-zag chain (**25**) with Pd···Pd separation of 3.191 (3) Å [224].



(25)

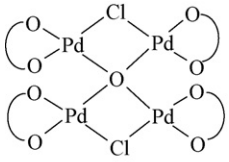
Reaction of [Pd(μ-X)(MeCN)R]$_2$ with Ph$_4$PX in CH$_2$Cl$_2$ results into formation of μ$_4$-X-bridged tetranuclear complexes [Pd$_4$R$_4$(μ-X)$_5$]$^-$ (X = Cl, Br, I; R = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$) (**26**) (structural type **XIX**), the chloro-bridged complex has been structurally characterized. The μ$_4$-Cl shows a pyramidalized geometry [225].



(X = Cl, Br, I; R = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$)

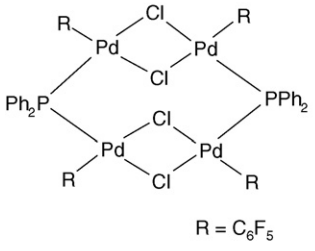
(26)

A μ_4-O bridged tetranuclear complex, $[Pd_4(\mu_4\text{-}O)(\mu\text{-}Cl)_2(dpm)_4]$ (**27**) has been isolated when $[Pd_2(\mu\text{-}OMe)_2(dpm)_2]$ was dissolved in CCl_4 and exposed in air. The μ_4-O has a distorted tetrahedral geometry and "$Pd_2Cl(\mu_4\text{-}O)$" rings are folded (structural type **XX**) [226]. Complexes containing tetrahedral tetradentate sulfido ligand (μ_4-S) have also been prepared [227]. Thus the reaction of $[Pd_2(\mu\text{-}OH)_2(C^{\frown}N)_2]$ with CS_2 in the presence of $HC^{\frown}N$ in dichloromethane yields a mixture of tri- and tetranuclear sulfido- bridged complexes, $[Pd_3(\mu_3\text{-}S)(\mu\text{-}OH)(C^{\frown}N)_3]$ and $[Pd_4(\mu_4\text{-}S)(\mu\text{-}OH)_2(C^{\frown}N)_4]$ ($(C^{\frown}N) = 4\text{-}EtOC_6H_3CH{=}N\text{-}C_6H_4Et\text{-}4$) [227]. The latter when treated with HCl affords the corresponding chloro-bridged derivative, $[Pd_4(\mu_4\text{-}S)(\mu\text{-}Cl)_2(C^{\frown}N)_4]$. The central ($\mu_4$-S) sulfido ligand acquires a distorted tetrahedral configuration.

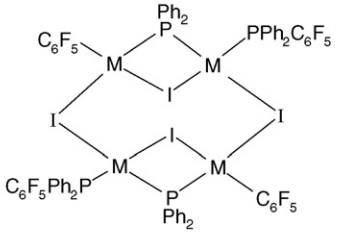


(27)

The reaction of $[Bu_4N]_2[Pd_2(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ with $PdCl_2$ in refluxing acetone gives a deep yellow tetranuclear phosphido-bridged complex, $[Bu_4N]_2[Pd_4(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)_4(C_6F_5)_4]$ (**28**) (structural type **XXI**) [228]. In the latter the two non-planar binuclear palladium fragments "$(C_6F_5)Pd(\mu\text{-}Cl)_2Pd(C_6F_5)$" are held together by PPh_2 bridges [228]. When a dichloromethane solution of $[M^{III}(\mu\text{-}PPh)_2(C_6F_5)_2I_2]$ is stirred at room temperature for long time, tetranuclear phosphido-bridged complexes $M_4(\mu\text{-}PPh_2)_2(\mu\text{-}I)_2(\mu\text{-}I)_2(C_6F_5)_2(PPh_2C_6F_5)_2]$ [29] are formed [229].

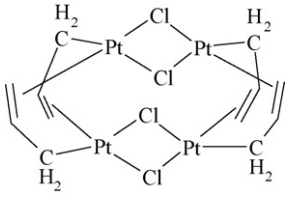


(28)



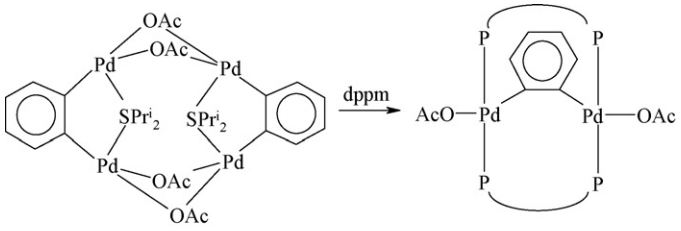
(29)

The reaction of diallylplatinum, $[Pt(\eta^3\text{-}C_3H_5)_2]$, prepared from $PtCl_2$ and allylMgCl [230], with anhydrous HCl yields a chloro(allyl)platinum(II) [231]. In contrast to its palladium analogue, the platinum complex is tetrameric, although higher allyl derivatives, $[Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$, are dimeric. The molecule has both chloro and allyl bridges (**30**) (structural type **XXII**). Each of the allyl group in the molecule is σ-bonded to one platinum while π-bonded to another platinum atom. The π-bonded olefin is perpendicular to the platinum square plane. The Pt···Pt distances ~ 3.27 (di-μ-C_3H_5) and ~3.23 Å (di-μ-Cl) are too long to account for any platinum–platinum interactions [231].



(30)

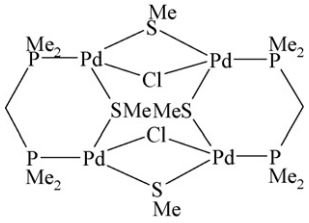
The complex **31** [232], formed from via C–H bond activation of benzene by $Pd(OAc)_2$-SR_2 system, undergoes a variety of reactions. With dppm or $PhCH_2SCH_2PPh_2$, binuclear 'A-frame' complexes are formed by bridge cleavage reaction (Eq. (24)) [233]:



(31)

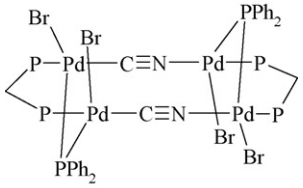
(24)

The reaction of $[Pd_2Cl_2(\mu\text{-}dmpm)_2(\mu\text{-}MeSC{\equiv}CSMe)]$, prepared by insertion of MeSC≡CSMe in $[Pd_2Cl_2(dmpm)_2]$, with $HBF_4{\cdot}Et_2O$ yields a tetranuclear palladium complex, $[Pd_4(\mu\text{-}SMe)_4(\mu\text{-}Cl)_2(\mu\text{-}dmpm)_2]$, (**32**) [234]. There are two types of Pd···Pd distances, one involving "$Pd_2Cl(SMe)$" (av 3.04 Å) and another "$Pd_2(SMe)(dmpm)$" (av 3.18 Å).



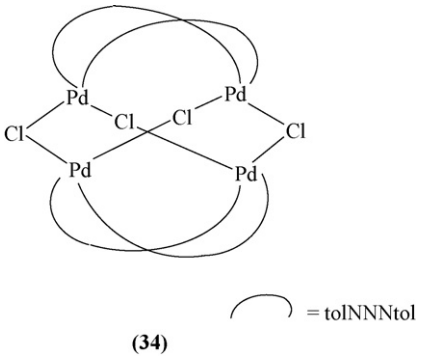
(32)

A tetranuclear palladium complex, $[\{Pd_2Br_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)\}_2(\mu\text{-}CN)_2]$ (**33**) has been prepared as a colorless crystalline solid in low yield (~10%) by the reaction between $[Pd_2(CH_2Bu^t)_2(\mu\text{-}Br)(\mu\text{-}dppm)_2]Br$ and $NaBH_3CN$ in THF [235]. The four Pd atoms, four P atoms of dppm and cyano ligands are almost planar and PPh_2 groups lie opposite side of this plane [235].



(33)

The reaction of Li_2PdCl_4 with 1,3-di-*p*-tolyltriazene in 1:1 molar ratio in refluxing methanol in the presence of sodium carbonate yields black crystals of a trizenedo-/chloro-bridged tetranuclear palladium complex, $[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}tolNNNtol)_4]$ (**34**) [236].



(34)

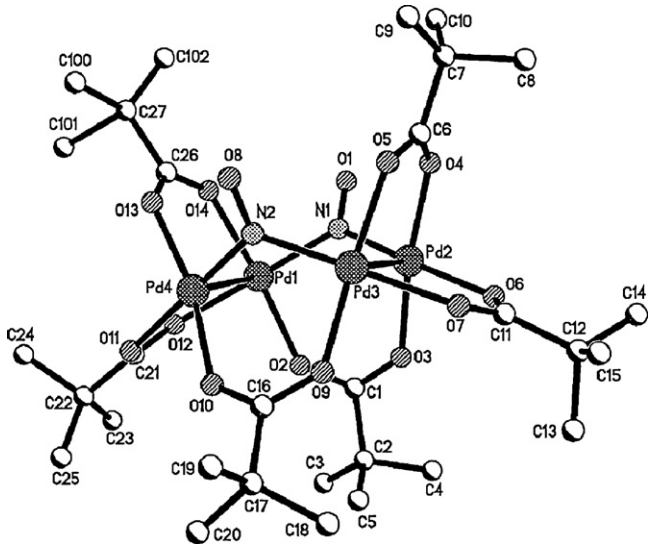


Fig. 17. Molecular structure of $[Pd_4(NO)_2(\mu\text{-}O_2CBu^t)_6]$; [238] (Reproduced with permission of Elsevier Ltd.).

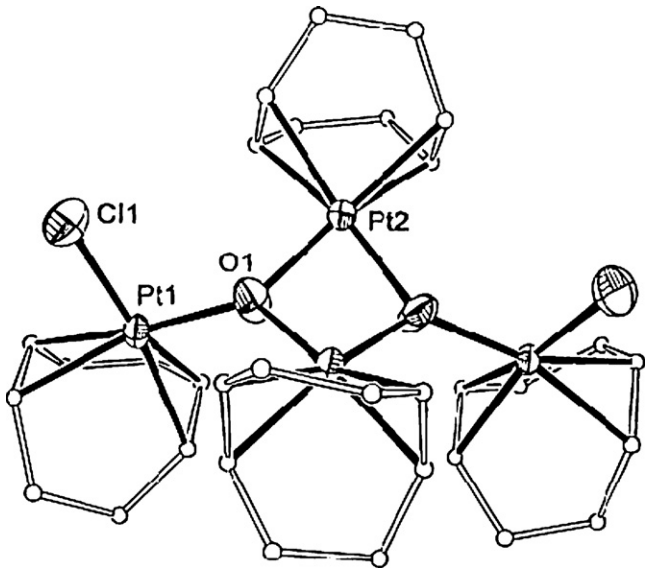
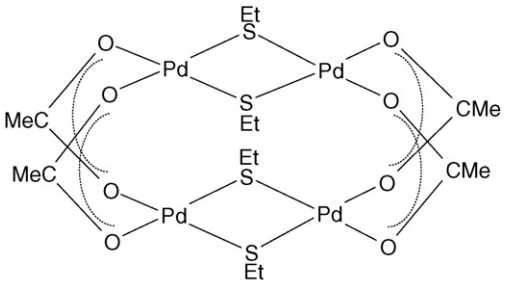


Fig. 18. Structure of $[(1,5\text{-}COD)_4Pt_4(\mu^3\text{-}O)_2Cl_2]^{2+}$; [246] (Reproduced with permission of American Chemical Society).

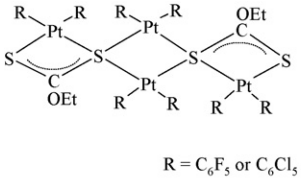
Palladium and platinum nitrosyl complexes, $[M_4(\mu\text{-}NO)_2(O_2CR)_6]$ have been reported [237–240]. The reaction of Pd(NO)Cl with silver carboxylate gives reddish brown nitrosyl complexes $[Pd_4(NO)_2(O_2CR)_6]$ (R = Me, Ph, Bz, Bu^t, CH_2Cl) [238]. The structures of palladium and platinum complexes are isomorphous having two bridging NO groups in *cis*-arrangement and six-bridging carboxylate groups. The four metal atoms form a M_4 rectangle with the pair of bridging ligands on each side of this rectangle (Fig. 17) [238–240]. The reaction of $K_2Pt(NO_2)_4$ with acetic acid yields $[Pt_4(\mu\text{-}OAc)_5(\mu\text{-}NO)_2(\mu\text{-}NO_2)]$ [241].

In $[Pd_4(SEt)_4(OAc)_4]$ four-palladium atoms form a planar cyclic structure (**35**) with Pd···Pd distances varying between 3.036 and 3.195 Å. The neighboring palladium atoms are bound by two acetate or two SEt bridges [242]. A phenylselenolato-bridged complex, $[Pd(\mu\text{-}SePh)(\mu\text{-}OAc)]_4$ has been isolated by a reaction between $[Pd(OAc)_2]_3$ and $(PhSe)_3Sn\text{-}(CH_2)_4Sn(SePh)_3$ in dichloromethane [243]. Similar cyclic tetranuclear complexes, $[Pd_4(\mu\text{-}OAc)_4\{\mu\text{-}C_6H_2(NR)_4\}_2]$ (R = CH_2Bu^t, Bz), have been isolated by the reactions of palladium acetate with azophenine [244].

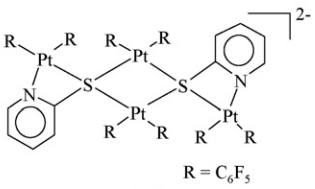


(35)

The reaction of $[Bu_4N][Pt(C_6X_5)_2(S_2COEt)]$ with *cis*-$[Pt(C_6X_5)_2(thf)_2]$ affords tetranuclear complexes, $[Bu_4N]_2[Pt_4(C_6X_5)_8(S_2COEt)_2]$ (X = F or Cl) (**36**) (structural type **XXIII**) in which xanthate ligand bridges three platinum atoms [245]. Reaction of $[Bu_4N][Pt(C_6F_5)_2(Spy)]$ either with *cis*-$[Pt(C_6F_6)_2(thf)_2]$ or with $[Bu_4N]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ in the presence of $AgClO_4$ affords a tetranuclear platinum complex, $[Bu_4N]_2[Pt_4(Spy)_2(C_6F_5)_8]$ as a colorless crystalline solid [30]. The pyridine thiolate sulfur atoms are tetra-coordinated involving all the three electron pairs in Pt–S bonding (**37**).

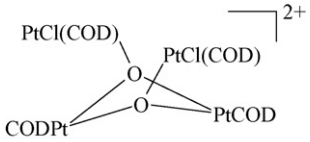


(36)



(37)

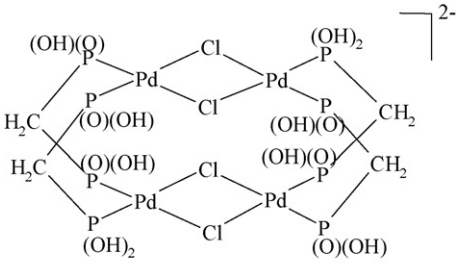
Reaction of $[(LAu)_3(\mu^3\text{-}O)][BF_4]$ with an excess of $CODPtCl_2$ in THF affords an oxo-bridged tetranuclear platinum complex $[(COD)_4Pt_4(\mu^3\text{-}O)_2Cl_2][BF_4]_2$ (**38**) (Fig. 18) and [AuLCl] (L = tertiary phosphine). The **38** exhibits fluxional behavior due to rotation of the CODPtCl fragments about Pt–O bonds. The Pt_2O_2 core is non-planar with the hinge angle of 28.7° and Pt–O distances of 2.018 (6) Å [246]. The complex **38** undergoes hydrolysis in moist solvents to yield another tetranuclear complex $[(COD)_4Pt_4(\mu^3\text{-}O)_2(\mu^2\text{-}OH)][BF_4]_3$ which has been structurally characterized [246]. The **38** reacts with olefin and triphenylphosphine leading to the formation of a mixture of products [247].



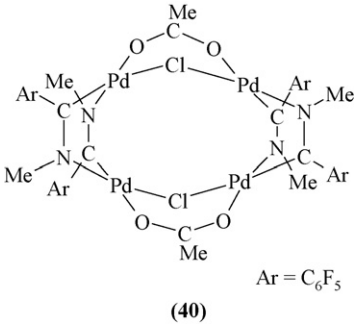
(38)

Complexes with cyclic structures have been prepared and characterized. Reaction of methylene bis(phosphinic acid) with Na_2PdCl_4 in methanol gives a yellow tetranuclear dianionic complex $[Pd_4Cl_4(CH_2P_2O_4H_2)_2(CH_2P_2O_4H_3)_2]^{2-}$ (**39**) in 10% yields (structural type **XXII**). The reaction in water under all pH conditions, however, results into the formation of palladium

metal [248]. The complex has bridging chloride as well as methylenebis(phosphinic acidate) ligands with Pd···Pd separation of 3.539 (1) Å (in Pd_2Cl_2 bridge) and 3.332 (1) Å (in $Pd_2(PCP)_2$) [248].



Imidoyl-bridged tetranuclear palladium complexes, $[Pd_2(\mu\text{-}Cl)_2\{\mu\text{-}C(C_6F_5)=NR'\}_2]_2$ have been prepared [249–251]. The bridging chloride is readily replaced by other bridging ligands, like OAc, CF_3COO, PhS, to yield homo- and hetero-bridged tetranuclear derivatives, $[Pd_2(\mu\text{-}X)(\mu\text{-}Y)\{\mu\text{-}C(C_6F_5)=NR'\}_2]_2$ (**40**) (X = Cl, OAc, CF_3COO; Y = OAc, SPh, *etc.*) [251].

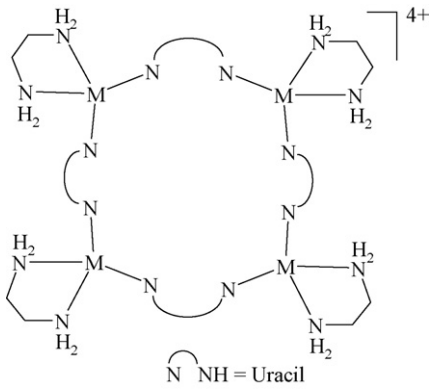


Reaction of $CODPtCl_2$ with *meso*-$(PhH(O)PCH_2)_2$ in the presence of sodium methoxide in methanol affords a colorless tetranuclear complex, $[Pt\{(R,S)\text{–}Ph(O)PCH_2CH_2P(O)Ph]_4$ in 75% yield. The mass spectrum exhibits an intense parent ion peak at *m/z* 1885 [252]. The X-ray structure reveals a cyclic tetramer in which four platinum atoms are held together by four phosphinito ligands each of which chelates through phosphorus while phosphoryl oxygens are coordinated to two adjacent platinum atoms [252].

Treatment of $[PdBr(4\text{-}Mepy)\{Ph_2P\text{–}C_6H_3O(OH)]$ with 48% HBr in acetone water mixture yields red crystals of a neutral tetranuclear complex $[PdBr\{Ph_2PC_6H_3(O)(OH)]_4$ together with the crystals of 4-Mepy·HBr and $[PdBr_2\{Ph_2PC_6H_3(OPPh_2)(OH)]$ [253]. In the former each palladium atom is coordinated by P, O chelate and the hydroquinone oxygen atom binds the adjacent palladium.

Cyclic tetranuclear palladium and platinum complexes, having structure similar to classical calix[4]arene, $[M(en)(N^{\cap}N)]_4[NO_3]_4$ (**41**) have been isolated by the reactions of $[(en)M(H_2O)_2][NO_3]_2$ with an appropriate nucleobase such as uracil, 2-hydroxypyrimidine [254–258]. The bridging nucleobases are arranged in a 1,3-alternating fashion. The tetranuclear cations are stacked along the crystallographic *z* axis. Although these complexes are structural analogs of calix[4]arenes, the coordination of their oxo-surface with various metal ions is rather weak [255,258]. The copper ions, however, coordinate with the oxo-surfaces of two tetranuclear cations [258]. The complex, $[Pt(en)(OH)]_4[NO_3]_4$, prepared by the reaction of $[Pt(en)Cl_2]$ with $AgNO_3$, is a hydroxo-bridged cyclic tetramer [259], rather than a dimer as thought previously based on an analogy with $[Pt_2(\mu\text{-}OH)_2(NH_3)_4]^{2+}$ [260].

The molecule $[Pt_4(\mu\text{-}CO_3)_2(NH_3)_8][NO_3]_4$ comprises of four-fused six-membered rings [261].



When $[Pd_2(\mu\text{-}Cl)_2Cl_2(PPr_3)_2]$ is treated with $NaNO_2$ in methanol a yellow tetranuclear complex, $[Pd_4\{\mu\text{-}ON(O)\}_4(NO_2)_4(PPr_3)_4]$ is formed in which square-planar palladium atoms are joined by nitro–nitrito bridges (Pd–O–N(O)–Pd) [262], while a nitro group and PPr_3 ligand complete the coordination around each palladium. The nitro–nitrito bridge in the complex can be cleaved by a variety of nucleophiles to afford mono- and binuclear complexes [263]. A similar cyclic structure is adopted by $[Pd_4(\mu\text{-}CN)_4(C_6F_5)_4(PEt_3)_4]$ [264]. The reaction of $[PdCl_2(PhCN)_2]$ with $LiCH_2SPh$ yields a cyclic tetranuclear dialkyl palladium complex, $[Pd(CH_2SPh)_2]_4$ in which CH_2SPh ligands bridge four-palladium atoms *via* sulfur and CH_2 group [265].

Halide abstraction in a mononuclear carbene complex by $Ag(O_2CCF_3)$ leads to the formation of cyclic tetranuclear complex $[PdMe(O_2CCF_3)(2\text{-}py\text{-}CH_2N\text{=}C\text{-}N\text{-}Me]_4$ in which carbene carbon and pyridine nitrogen forms Pd–N···C–Pd bridges [266].

The lone pair of sulfur atom in $[Pd(aet)_2]$ is sufficiently basic and has been exploited in constructing bi-, tetra- and hexanuclear complexes. The reactions of $Pd(aet)_2$ with $[Pd(NO_3)_2(diimine)]$ in water afforded tetranuclear complexes, $[\{Pd(diimine)\}_2\{Pd(aet)_2\}_2]^{4+}$ (diimine = bipy, Me_2bipy, phen, Me_2phen) (structural type **XXIII**) (Fig. 19) [267,268]. All these complexes have been structurally

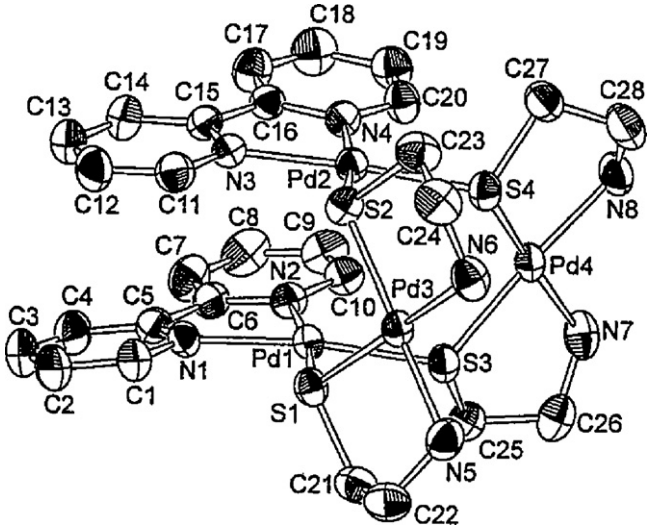
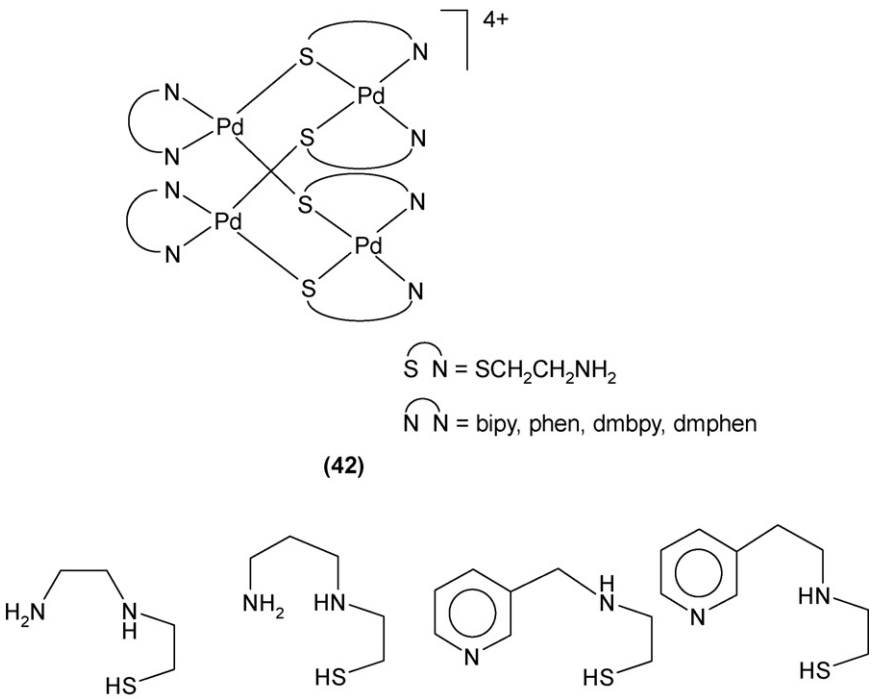


Fig. 19. Molecular structure of $[\{Pd(bipy)\}_2\{Pd(aet)_2\}_2]^{4+}$; [267] (Reproduced by permission of Chemical Society of Japan).



Scheme 11.

characterized. The PdN_2S_2 planes of $Pd(aet)_2$ are perpendicular to those in the "Pd(N∩N)" fragments which are coordinated to two sulfur atoms from different $Pd(aet)_2$ units (**42**). The N∩N ligands are aligned in such a way so as to overlap each other [268]. The Pd–S distances in $Pd(aet)_2$ moiety are slightly shorter than observed in $[Pd(N^{\cap}N)S_2]$ units. Another variant of tetranuclear palladium complexes with eight-membered Pd_4S_4 core and N_2S_2 coordination environment around each palladium center has been isolated by the reactions of Na_2PdCl_4 with tridentate thiols containing NNS donor set (Scheme 11) [269,270]. Reaction of $[Pd(Spy)_2]_2$ with iodine in chloroform yields bis(2-pyridyl)disulfide and a tetranuclear palladium complex, $[Pd_4I_2(Spy)_6]$ rather than the expected binuclear palladium(III) complex, $[Pd_2I_2(Spy)_4]$ [271]. The four-palladium atoms in the complex are disposed in a rhombic fashion and are bridged by Spy ligands [271]. The electro-neutral complexes with a Pd_4S_4 core have also been prepared using dianionic thiosemicarbozene ligands [272–274]. The Pd_4S_4 eight-membered ring in $[Pd_4(TSDO)_4]\cdot 4H_2O\cdot 4DMF$ (H_2TSDO = 6-amino-5-formyl-1,3-dimethyluracil-thiosemicarbozene) has a boat like conformation [272]. A similar tetranuclear neutral complex, $[PdCl(SCH_2CH(COOH)(NH_2)]_4$, with cysteine has been reported [275], although based on IR data binuclear structure was proposed [276]. The cysteine acts as a tridentate ligand and bridges two-palladium atoms. The S_2NCl donor atoms define coordination around each palladium atom [275].

The complex $[PdI_2\{o\text{-}C_6H_4(TeMe)_2\}]$ on heating in dmso leads to monodemethylation with concomitant formation of a poorly soluble black tetranuclear telluorolate complex, $[PdI(TeC_6H_4TeMe\text{-}2)]_4$ (Fig. 20) in which eight-membered Pd_4Te_4 ring has a "cradle" configuration [277].

Reactions between $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}RC_3H_4)_2]$ and bis-imidazole (H_2bim)/2,2′-bisbenzimidazole (H_2bzim) in the presence of KOH in 1:1 molar ratio give tetranuclear complexes, $[Pd_4(\eta^3\text{-}RC_3H_4)_4(\mu\text{-}L)_2]$ (R = H or Me; L = bim or bzim) [278]. The latter can also be obtained by treatment of $[Pd(\eta^3\text{-}RC_3H_4)(acac)]$ with H_2bim/H_2bzim in dichloromethane–methanol. The structure of $[Pd_4(\eta^3\text{-}C_6H_5)_4(\mu\text{-}bim)_2]$ has been established by X-ray crystallography [278]. The molecule has a "butterfly shape" and the bim acts as an unsymmetrical tetradentate bridging ligand (**43**).

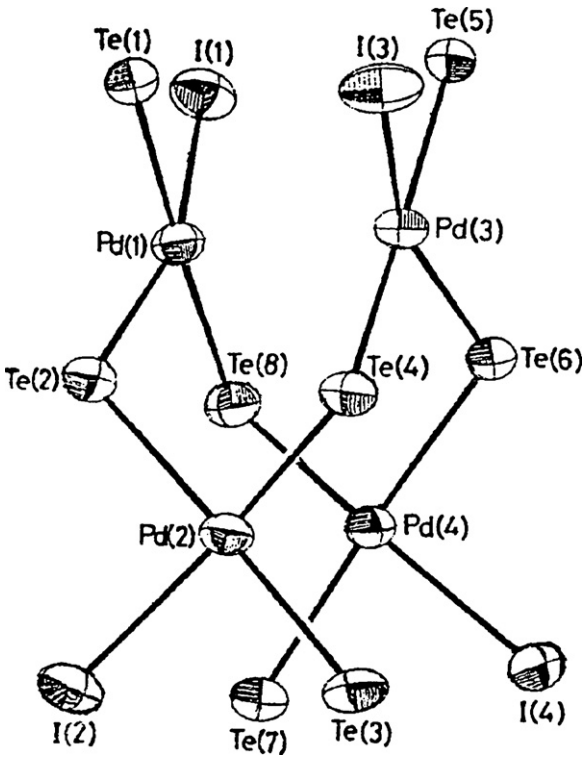
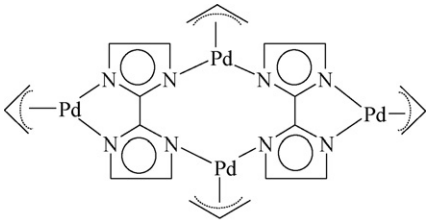


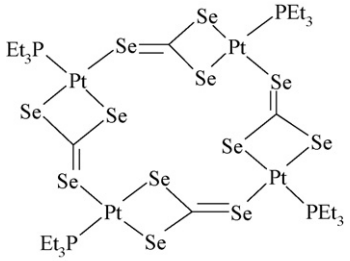
Fig. 20. Heavy atom framework of $[PdI(TeC_6H_4TeMe\text{-}2)]_4$; [277] (Reproduced with permission of American Chemical Society).

The reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ with Li_2pyS_2 in THF yields $[Pd_4(\mu\text{-}pyS_2)_2(\eta^3\text{-}C_3H_5)_4]$ [279].



(43)

Although reaction of $PtCl_2(PR_3)_2$ (PR_3 = PMe_3, PMe_2Ph, PPh_3, 1/3 dppp, *etc.*) with CSe_2 in liquid ammonia affords mononuclear triselenocarbonate complexes, $[Pt(Se_3C)(PR_3)_2]$, when PR_3 is PEt_3 a tetranuclear complex, $[Pt_4(Se_3C)_4(PEt_3)_4]$ forms with the elimination of Et_3PSe [280]. All the three selenium atoms of the triselenocarbonate groups are coordinated to platinum resulting into a puckered 16-membered ring (**44**) [280]. Reaction of $Pd(hfac)_2$ with 0.5 equivalent of urea in methanol affords orange crystals of a ureido bridged tetranuclear complex $[Pd_4(hfac)_4(\mu\text{-}NHCONH)_2]$. The hfac ligand in the latter can be exchanged by acac [281]. Alkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 1,3- or 1,4-dibromobenzene yields overhead-bridged dialkylated products, $[(PPh_3)_4Pt_2(\mu\text{-}S)(\mu\text{-}SC_6H_4S)(\mu\text{-}S)Pt_2(PPh_3)_4]^{2+}$ [282].



(44)

3.2. Tetranuclear palladium and platinum carboxylates

The chemistry of platinum(II) carboxylates has been reviewed recently by Yamaguchi and Ito [283]. Preparation of palladium and platinum(II) acetates was described by Wilkinson and coworkers in 1965 [282] who suggested trimeric structure for both the complexes. However, X-ray structural analysis of platinum diacetate by Skapski in 1976 has revealed a tetrameric structure [284].

Platinum carboxylates, such as $[Pt(OAc)_2]_4$ [285], $[Pt(O_2CCF_3)_2]_4$ [286] and $[Pt_4(OAc)_4(H_2O)_8]^{4+}$ [287] are usually obtained by reducing higher valent platinum compounds like $PtCl_4$, $K_2Pt(OH)_6$, $K_2[Pt_2(SO_4)_4(H_2O)_2]$. The reaction of $[Pd(O_2CR)_2]_3$ (R = Me, CF_3, CCl_3, C_5H_{11}) with 80% *tert*-butylhydroperoxide yields orange crystalline tetranuclear *tert*-butyl peroxy complexes, $[Pd(\mu\text{-}O_2CR)(OOBu^t)]_4$ [288].

X-ray structural analyses of $[Pt_4(O_2CR)_8]$ (R = Me, CF_3, Bu^t) [284,286,289–291] showed that four octahedral platinum atoms form a square-planar core with short Pt–Pt distances of ~2.5 Å. The platinum atoms are held together by eight bridging carboxylate ligands (Fig. 21). The four-carboxylate groups are nearly coplanar with the Pt_4 core while the remaining four carboxylates lie alternately above and below this core. The Pt–O distances for the coplanar carboxylate groups are slightly longer than those for out-of-plane

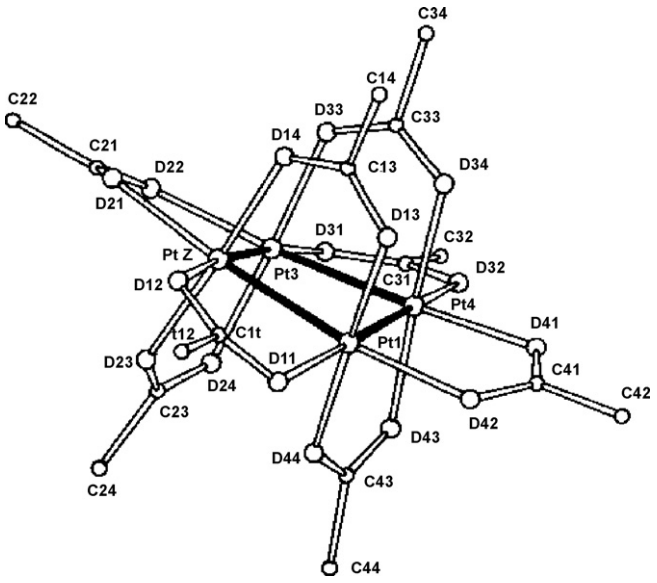


Fig. 21. Molecular structure $[Pt_4(OAc)_8]$; [290] (Reproduced with permission of IUCr).

ligands. The acetate, $[Pt_4(OAc)_8]$ can be isolated in tetragonal [289] and monoclinic forms [290] on crystallization from glacial acetic acid.

In-plane acetate ligands in $[Pt_4(OAc)_8]$ are labile owing to strong *trans* influence of the Pt–Pt bond, while out-of-plane acetate groups are inert to substitution [292]. However, in case of $[Pt_4(O_2CCF_3)_8]$ all the eight trifluoroacetates can be replaced by pivalate ligands due to poor basicity of CF_3CO_2 group [286]. The labiality of in-plane acetate groups in $[Pt_4(OAc)_8]$ has been exploited for the preparation of several substituted products. Depending on the nature of incoming ligand, both trinuclear (triangular, *vide supra*) and tetranuclear complexes have been isolated and in most of the cases, have been characterized by X-ray crystallography. The tetranuclear platinum complexes retain their parent Pt_4 core with Pt–Pt distance of ~2.5 Å (Table 7). The reactions with anionic ligands (LH) (*e.g.*, RCO_2; R = CF_3, CCl_3, Ph, CH=CH_2 [292–294], 2-py [295], $(EtO)_2PS_2$ [296], proline [297], glycine [298], acac [299], amidine [300]) are quite facile and yields tetra-substituted complexes (Eq. (25)). The reaction with acetamidine was investigated and sequentially substituted complexes, $[Pt_4(OAc)_{8-n}(MeCONH)_n]$ (n = 1–4) have been identified by ^{195}Pt NMR spectroscopy [301]. In-plane acetate ligands can also be substituted sequentially by neutral nitrogen donor ligands (*e.g.*, py, 4-Me_2Npy, en) to give tetranuclear ionic complexes, $[Pt_4(OAc)_4(py)_4]^{2+}$, $[Pt_4(OAc)_4(N^{\frown}N)_4]^{4+}$ [287,295,298,302]:

$$[Pt_2(OAc)_8] + 4LH \rightarrow [Pt_4(OAc)_4(L)_4] + 4AcOH\cdots \quad (25)$$

The $[Pt_4(OAc)_8]$ is photoluminescent both in the solid state and in solution and exhibits emission bands at 510 and 630 nm. The red emission (λ_{max} 630 nm) has a longer life (τ = 1.8 μs) than the blue emission band (τ = 5 ns) and is partially quenched in the presence of air [303]. It has been suggested that the Pt–Pt bonds are weakened in the emissive excited state [303]. The $Pt_4(OAc)_8$ has been used as a catalyst for hydrolysis of acetonitrile to acetamide [304] and for decomposition of formic acid to CO_2 and H_2 [305]. The $[Pd_4(OAc)_4(OOBu^t)_4]$ are efficient reagents for oxidation of terminal olefins to methyl ketone [288].

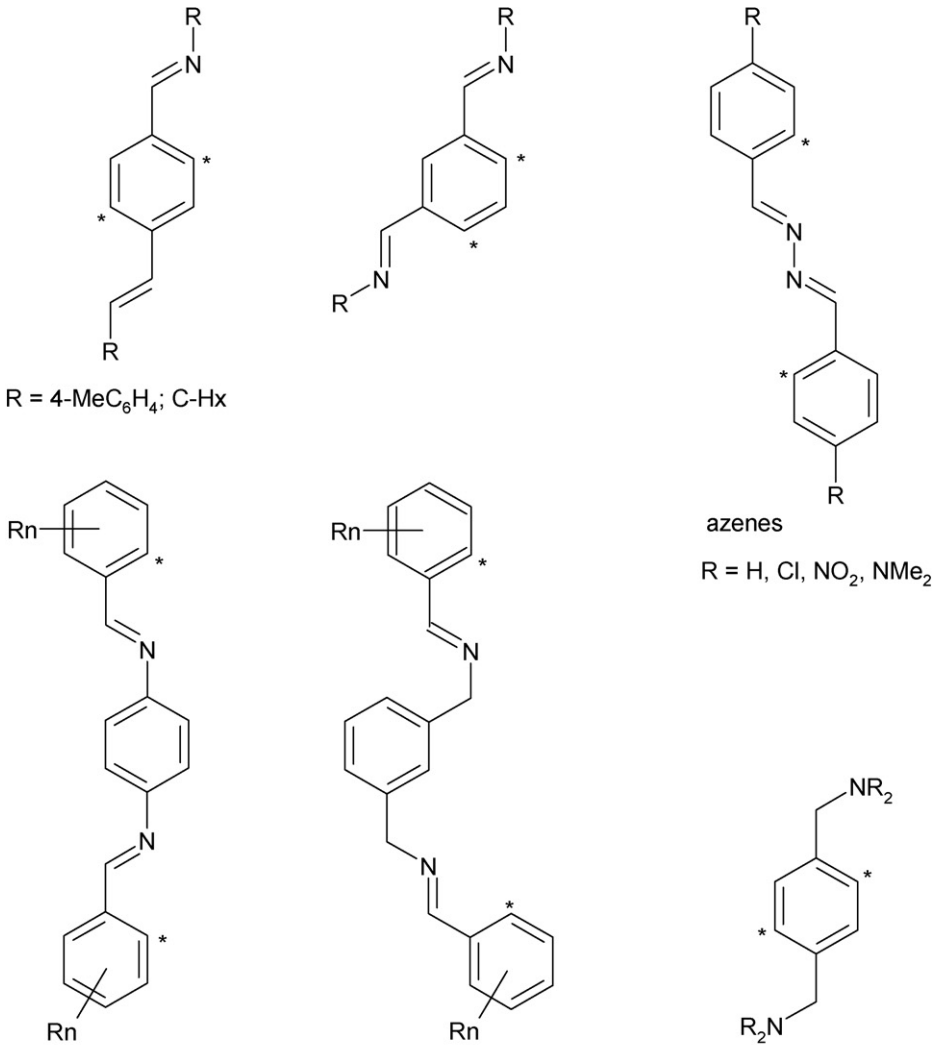
Table 7
Tetranuclear palladium(II) and platinum(II) carboxylate complexes characterized by X-ray crystallography.

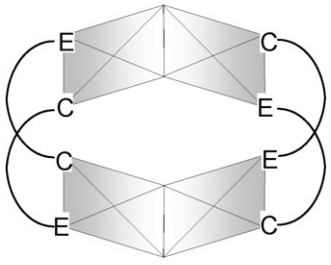
Complex	Comments	Reference
$[Pt_4(\mu\text{-}OAc)_8]$ (tetragonal)	Pt–Pt = 2.492 (1)–2.498 (1) Å Pt–O = 1.97 (1)–2.02 (1) Å 2.13 (1)–2.18 (1) Å	[289] [290]
(monoclinic)	Pt–Pt = 2.493 (1)–2.501 (1) Å Pt–O = 2.00 (1)–2.02 (1) Å 2.14 (1)–2.18 (1) Å	
$[Pt_4(O_2CCF_3)_8]$	Pt–Pt = 2.503–2.513 Å Pt–O = 1.994–2.175 Å	[286]
$[Pt_4(O_2CBu^t)_8]$		[291]
$[Pt_4(\mu\text{-}OAc)_4(\mu\text{-}O_2CCCl_3)_4]$	Pt–Pt = 2.49 Å Pt–O (OAc) = 2.00–2.01 Å Pt–O (O_2CCCl_3) = 2.14 (5)–2.20 (4) Å	[292]
$[Pt_4(\mu\text{-}OAc)_4\{S_2P(OEt)_2\}_4]$		[296]
with bridging dithiophosphate	Pt–Pt = 2.58 (av) Å	
with chelating dithiophosphate	Pt–Pt = 2.573 (1) Å	
$[Pt_4(\mu\text{-}OAc)_4(\mu\text{-acac-O, C}^3)_4]$	Pt–Pt = 2.578 (1), 2.595 (1) Å Pt–O (OAc) = 2.01 (2)–2.03 (2) Å	[299]
$[Pt_4(\mu\text{-}OAc)_4(\mu\text{-pro})_4]$ (proH = L-proline)	Pt–Pt = 2.531 (1)–2.537 (1) Å	[297]
$[Pt_4(\mu\text{-}OAc)_6(\mu\text{-DBuPhBp})]$	Two in-plane acetates are replaced by bisamidinate ligand	[300]
(DBuPhBp = 1,3-bis(*p-tert*-butylphenylbenzamidinate)propane)	Pt–Pt = 2.513 Å	
$[Pt_4(OAc)_4(pic)_4]$	Pt–Pt = 2.546 (1)–2.555 (1) Å	[295]
$[Pt_4(OAc)_4(glycinate)_4]$	Pt–Pt = 2.530–2.538 (1) Å	[283]
$[Pt_4(OAc)_4(en)_4]^{4+}$	Pt–Pt = 2.557 (1)	[295]
$[Pt_4(OAc)_4(py)_4]^{2+}$	Pt–Pt = 2.522 (5)–2.525 (3)	[287]
$[Pt_4(OAc)_4(dmap)_4]^{2+}$	Pt–Pt = 2.530 (1), 2.545 (1) Å	[298]
$[Pt_4(OAc)_4(dmap)_8]^{4+}$	Pt–Pt = 2.577 (2) Å	[298]
$[Pd_4(O_2CCCl_3)_4(OOBu^t)_4]$	Pd–Pd = 2.91 Å	[288]

3.3. Tetranuclear complexes with cyclometalated ligands

Cyclometalation has been one of the important families of reactions studied extensively for more than four decades. Cyclometallated compounds find numerous applications in organic synthesis, catalysis, materials science and bio-sciences. Cyclopalladated compounds are usually prepared by a reaction between Na_2PdCl_4 or $[Pd(OAc)_2]_3$ and an organic ligand in aqueous/organic solvent medium. The reaction yields binuclear complexes of general formula, $[Pd_2(\mu\text{-}X)_2(E^{\cap}C)_2]$ (X = Cl or OAc; E = N, P, *etc.*) which are isolated as *cis* and/or *trans* isomers with a boat conformation for the eight-membered "$Pd_2(OAc)_2$" (when X = OAc) ring and either planar or non-planar four-membered "$Pd_2(\mu\text{-}Cl)_2$" (when X = Cl) ring. As an extension of this reaction, double metalation of certain ligands containing at least two donor atoms has also been explored. Accordingly a variety of ligands, such as Schiff bases [306–322], benzylamines [323,324], azenes [325,326], N-heterocycles [327,328], ferrocenyl imines [329,330], bis-iminophosphoranes [331], *etc.* (Scheme 12) have been metalated. Double metalation usually leads to the formation of insoluble bridged complexes. Structural studies (Table 8), when possible, have revealed their tetrameric structure in which two binuclear fragments are linked by binuclear cyclometalated ligands (**XXV**). These complexes in general, undergo reactions shown by binuclear cyclometalated complexes. These reactions include bridge cleavage by neutral donor ligands (*e.g.*, pyridine, bipyridine, tertiary phosphines) [308,310,312,314,317–319,321,324,325,332], substitution of bridging ligands by another anionic ligand (*e.g.*, Cl, Br, OAc, N_3, SCN) [307,319,325,326] and substitution resulting in bridge cleavage (*e.g.*, by acac) [308,310,315,317,324,328]. Tetranuclear complexes derived from Schiff base ligands exhibit mesomorphic properties [311,315,316,320].

Double palladation of benzylidene arylamines (**45**) [322,333,334] affords tetranuclear complexes in which four nearly planar "$[Pd(OC_6H_4N{=}CHAr)]$" fragments share oxygen atom of the neighbouring unit to form a non-planar (Pd_4O_4) eight-membered ring of alternating Pd and O atoms (**46**). Each palladium atom is coordinated to an aryl carbon, a C=N nitrogen, phenoxy oxygen and also to a bridging oxygen atom of a neighbouring ligand. Thiosemicarbazones and related ligands such as $RC_6H_4CR'{=}NN(H)C(=S)NHR$ "(R = 4-Me, H; R′ = Me or Et; R″ = H or Me) [275,335,336], react with K_2PdCl_4 to give tetranuclear palladium complexes $[Pd\{RC_6H_3CR''{=}NN{=}C(S)NHR''\}]_4$ in which metalated ligands acts in a tridentate fashion (C, N, S) [335]. Reaction of 3,5-diacetyl-1,2,4-triazole bis(4-ethylthiosemicarbazone) (H_5L) reacts with Li_2PdCl_4 in methanol to give an orange dimeric complex $[\{Pd(\mu\text{-}H_3L)\}_2]$ which on recrystallization from dmso affords a disulfide-bridged tetranuclear complex, $[\{Pd_4(\mu_2\text{-}\eta^2\text{-}S_2)H_2L)_2]$ in which the disulfide ligand is thought to be formed by the oxidation of some ligands [275]. The disulfide ligand bridges two planar subunits of $[Pd_2(H_2L)]^+$. The complex $[Pd_2\{1,3\text{-}(CH{=}NCH_2C_4H_7O)_2C_6H_2\}(\mu\text{-}Cl)Cl(PPh_3)]_2$ is unusual in a sense





(XXV)

Scheme 12.

Table 8
X-ray structural data on tetranuclear cyclometalated complexes.

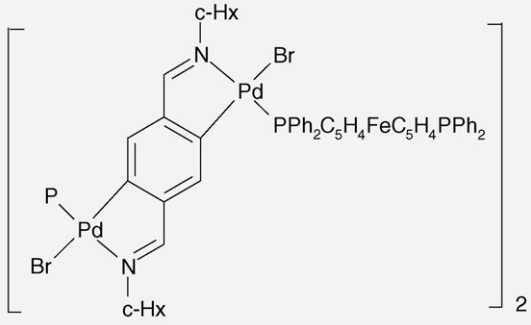
Complex	Comments	Reference
$[\{Pd_2(\mu\text{-}Br)_2\}_2\{1,4\text{-}(4,5,6\text{-}(MeO)_3C_6HCH{=}N)_2C_6H_4\}_2]$	Pd···Pd = 3.662 (5) Å Pd–Br = 2.443 (3)–2.564 (4) Å Pd–C = 1.992 (6) Å The molecule has a planar structure	[309]
$[\{Pd_2(\mu\text{-}I)_2\}_2\{(C_6H(4,5,6\text{-}OHx)_3CH{=}N\}_2C_6H_4\}_2]$	Pd···Pd = 3.888 (2) Å Pd–I = 2.72 (1), 2.58 (1) Å $Pd_2(\mu\text{-}I)_2$ fragaments are planar	[311]
$[Pd_2\{1,3\text{-}[CH{=}NCH_2C_4H_7O]_2C_6H_4](\mu\text{-}Cl)(PPh_3)]_2$		[320]
	Pd–C = 2.032–2.004 (6) Å Pd–Br = 2.4971 (8)/2.5157 (9) Å	[332]
$[Pd(OC_6H_4N{=}CHC_6H_4]_4$	Pd···Pd = 3.22 Å	[333]
$[Pd(OC_6H_4N{=}CHC_6H_2(Me)_2CH_2]_4$	Pd–O = 2.045 (3)–2.130 (3) Å Pd–N = 1.97 (av) Å Pd–C = 1.99 (av) Å	[334]
$[Pd\{\kappa^2(C,O)\text{-}\mu\text{-}C(=Nxyl)C_6H_4O\text{-}2\}(CNxyl)]_4$	Pd–C = 1.926 (5)–2.004 (4) Å Pd–O = 2.052 (3), 2.195 (3) Å	[337]
$[Pd\{\kappa^3(C,N,O)\text{-}\mu_2(O)\text{-}C_6H_4(CHMeN{=}CHC_6H_4O\text{-}2)\text{-}2\}]_4$	Pd–C = 1.96 (1) Å Pd···Pd = ≥ 3.47 Å	[338]
$[Pd\{\kappa^2(P,O)\text{-}\mu\text{-}(O)\text{–}Ph_2P(C_6H_3(OH)\text{-}3\text{-}O\text{-}6\}Br]_4$		[253]
$[Pd\{OC(O)C_6H_4\}(PPh_3)]_4$	Pd–C = 1.95 (3) Å Pd–O = 2.06, 2.16 (2) Å cyclic tetramer	[339]
$[Pd(1\text{-}nabz)]_4$	Pd···Pd = 3.180 (1) Å	[340]
1-nabz = 2-N-(1-naphthylmethylideneamino)benzenethiolato	Pd–C = 2.014 (8) Å Pd–S (bridging) = 2.317 (2) Å (terminal) = 2.365 (2) Å	
$[Pt(1\text{-}nabz)]_4$	Pt···Pt = 3.210 (3) Å Pt–C = 2.00 (3) Å Pt–S (bridging) = 2.316 (8) Å (terminal) = 2.350 (8) Å	[340]
$[Pt_4(Phbt)_4]$	Pt···Pt = 3.282 (3) Å	[343]
$[Pd(phbz)]_4$	Pd···Pd = 3.299 (2), 3.334 (2) Å	[342]
phbz = 2-(phenylmethylideneamino) benzenethiolato	Pd–C = 2.011 (13) Å Pd–S bridging =	
$[\{Pd_2(\mu\text{-}OAc)_2\}_2\{1,4\text{-}(C_6H_4NCS)_2C_6H_4\}_2]$	Pd···Pd = 2.8810 (7) Å Pd–C = 1.972 (av) Å Pd–O = 2.047 (4)–2.148 (4) Å Counter hinged molecular box	[344]
$[\{Pd_2(\mu\text{-}O_2CCH_2OH)_2\}_2\{1,3\text{-}(C_6H_4NCNEt)_2C_6H_4\}_2]$	Pd–C = 1.942 (8) (av) Å Pd···Pd = 2.886 (1) Å	[345]

Table 8 (*Continued*)

Complex	Comments	Reference
$[Pd_4(\mu\text{-}OAc)_4\{1,4\text{-bis}(2\text{-pyridyloxy})\ phenylene\}_2]$	Pd···Pd = 2.918 (1) Å Pd–C = 1.97 (av) Å Pd–O = 2.052–2.171 Å	[347]
$[Pd\{2,3,4\text{-}(MeO)_3C_6HCH{=}N(2\text{-}O\text{-}5\text{-}Bu^tC_6H_3\}]_4$	Pd···Pd = 3.39 (av) Å	[322]
$[Pd\{5\text{-}Me\text{-}2\text{-}CH_2C_6H_3CH{=}N(2\text{-}OC_6H_4)\}]_4$	Pd···Pd = 3.23 (av) Å	[322]
$[Pd\{2\text{-}O,4,6\text{-}(MeO)_2C_6H_2CH{=}N(2\text{-}OC_6H_4)\}]_2$	Pd···Pd = 3.08 (av) Å	[322]
$[Pd\{C_6H_4C(Et){=}N{-}N{=}C(NH_2)S\}]_4$	Pd···Pd = 3.375 (9) Å Pd···Pd = 3.434 (9) Å	[335]
$[Pd_4(\mu_2\text{-}\eta^2\text{-}S_2)(H_2L)_2]$	S–S = 2.125 (18) Å	[275]
$[Pd_4(\mu_2\text{-}\eta^2\text{-}S_2)(H_2L)_2]$ H_5L = 3,5-bis(EtNH–C(=S)–N(H)–N=C(Me)–) triazole	Pd–S = 2.254 (15)–2.310 (15) Å Pd–N = 1.997 (5)–2.028 (5) Å	
$[\{Pd_2(\mu\text{-}OH)(\mu\text{-}OAc)\}_2\{2,3\text{-}(OC_5H_4N)_2C_{10}H_4\}_2]$	Pd–C = 1.978 (3) Å Pd···Pd = 3.043 (av) Å μ-OH trans to N four, six-membered chelate rings have boat conformations	[348]
$[Pd_2(\mu\text{-}OAc)\}_2\{1,3\text{-}(2\text{-}py)_2C_6H_2\}]_2$	Pd···Pd = 2.8460 (5), 2.9548 (6) Å Pd–C = 1.959 (5) Å Open book structure	[349]
$[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}CHC_6H_4NMe\text{-}2)_2(SEt_2)_2]_2$	Pd–C = 1.94 (2), 2.02 (2) Å Pd–Cl = 2.328 (5)–2.496 (4) Å Pd···Pd = 2.780 (2) Å	[350]
$[\{Pd_2(\mu\text{-}Cl)_2\}_2\{Me_2NCH_2C_6H_4Si(Me_2)CH_{2\text{-}})_2\}_2]$	Pd–Cl = 2.3105 (14)–2.4747 (14) Å Pd–C = 1.99 (av) Å Pd–N = 2.073 (av) Å	[351]
$[\{Pd(\mu\text{-}Cl)\{Me_2NCH_2C_6H_4\text{-}SiMe_2CH_2CH_2\}_4Si]$	Pd–Cl = 2.334 (2)–2.465 (2) Å Pd–C = 1.66 (av) Å Cl–Pd–Cl = 85.72° chloride bridged structure	[352]
$[Pd(\mu\text{-}Cl)(PhSCHCH_2C_6F_5)]_4$	Pd–C = 2.036 (8), 1.849 (9) Å Pd–Cl = 2.392 (2)–2.469 (2) Å Pd···Pd = 2.917 (2) Å	[353]
$[Pd_4Cl_2(phgly\text{-}O,N,C)_2(phgly\text{-}O,O)_2]^{2-}$	Pd···Pd = 3.127 (1)–4.513 (2) Å	[354]
$[Pd_4Cl_2(tolgly\text{-}O,N,C)_2(tolgly\text{-}O,O)_2]^{2-}$	Pd···Pd = 3.101 (1)–4.464 (1) Å	[354]
$[Pd(\mu\text{-}Br)(\mu\text{-}C_6H_4PPh_2)]_4$	Pd–Br = 2.505 (1), 2.567 (1) Å Pd–C = 2.023 (8) Pd···Pd = 3.64 Å	[355]
$[Pd(\mu\text{-}Cl)(\mu\text{-}C_6H_4PPh_2)]_4$	Pd···Pd = 3.58 Å Pd–Cl = 2.4007 (7), 2.4576 (18) Å Pd–C = 2.019 (3) Å	[356]
$[\{Pd_2(O_2CCF_3)_2\}_2\{C_6H(2\text{-}Me)(OPPh_2)_2\text{-}1,3\}_2]$	Pd–C = 1.996 (3),1.992 Å Pd–O = 2.141 (2), 2.145, 2.149, 2.151 (2) Å Pd···Pd = 3.2190 (3) Å	[357]
$[\{Pd_2(\mu\text{-}Cl)_2\}_2\{Ph_2PCH(CHP(Ph)\ CHCMeCMe)\}_2]$	Pd–C = 2.078 (10) Å Pd–Cl = 2.489 (3), 2.487 2.458 (3), 2.472 (3) Å Pd···Pd = 3.0161 (13), 2.9945 (13) Å	[375]

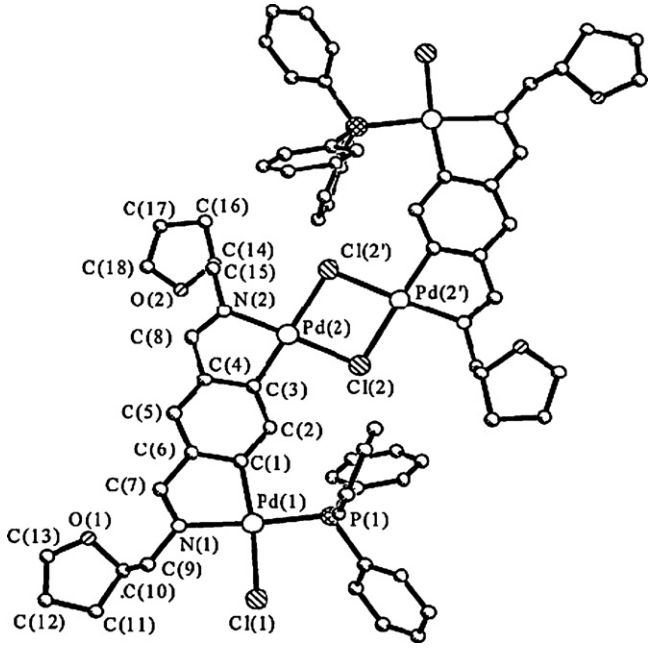
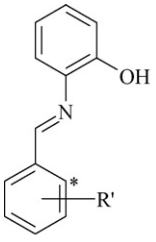
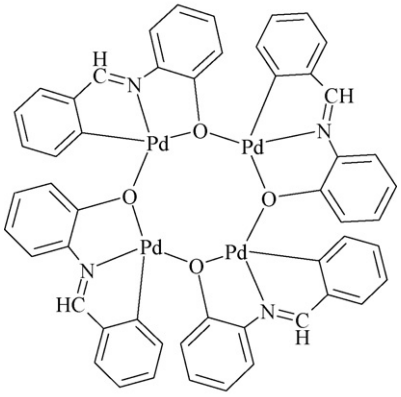


Fig. 22. Structure of $[Pd_2\{1,3\text{-}(CH{=}NCH_2C_4H_7O]_2C_6H_2\}(\mu\text{-}Cl)Cl(PPh_3)]_2$; [320] (Reproduced by permission of The Royal Society of Chemistry (RSC) for the Centre National de la Recherche Sceintifique (CNRS) and the RSC).

that it contains a binuclear "$Pd_2(\mu\text{-}Cl)_2$" fragment which is linked to two mononuclear palladium atoms, each coordinated to a chelated Schiff base, a chloride and PPh_3 ligand (Fig. 22) [320].



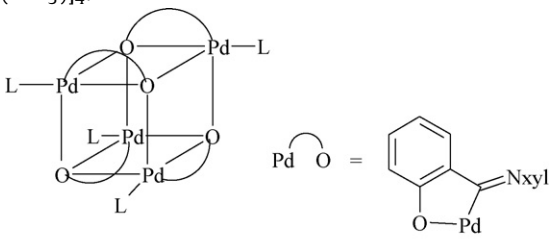
(45)



(46)

The reaction of $[Pd(I)(CNxyl)_2\{xylN{=}C(C_6H_4OH)\}]$ with palladium acetate in 2:1 stoichiometry in acetone gives a mixture of $[PdI_2(CNxyl)_2]$ and a tetranuclear palladium complex [337]. In the latter complex each palladium atom has chelating C,O-iminoacylphanolato ligand, NCxyl and oxygen atom of an adjacent fragment, $[Pd\{K^2(C,O)\mu\text{-}C(\text{-}Nxyl)C_6H_4O\text{-}2\}(CNxyl)]_4$ (**47**) [337]. A similar structure containing chelating (E–X–Y–O) core has been reported for $[Pd(K^3(C,N,O)\mu_2\text{-}(O)\text{-}C_6H_4(CHMeN{=}CHC_6H_4O\text{-}2\}\text{-}2]_4$ [338] and $[Pd\{K^2(P,O)\text{-}\mu\text{-}(O)\text{-}Ph_2P(C_6H_3(OH)\text{-}3\text{-}O\text{-}6\}Br]_4$ [253]. All these molecules are comprised of distorted cubic array of alternating palladium and oxygen atoms.

The reactions of 2-bromobenzaldehyde with $[Pd(PPh_3)_4]$ yields an oxidative addition product, *trans*-$[PdBr(C_6H_4CHO)(PPh_3)_2]$ which on treatment with cerium carbonate and $AgBF_4$ in thf results into oxidation of formyl group with the formation of a tetranuclear complex, $[Pd\{O_2CC_6H_4\}(PPh_3)]_4$ (**48**) [339]. The latter is also obtained by oxidative addition of 2-bromobenzoic acid to $[Pd(PPh_3)]_4$.



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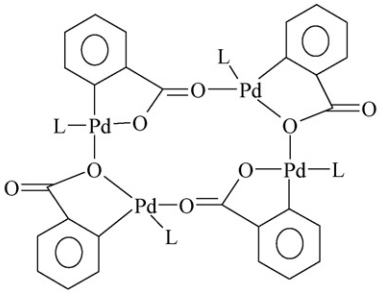
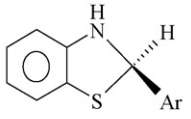


$L = PPh_3$

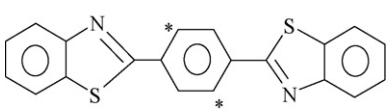
(48)

To study C–H activation and M···H–C agostic interactions, reactions of $Pd(OAc)_2$ with 2-(arylbenzothiozoline) (**49**) (aryl = phenyl or 1-naphthyl) have been carried out. Both mononuclear, $[Pd(HArbz\text{-}N,S)_2]$, and tetranuclear $[Pd(Arbz\text{-}C,N,S)]_4$, depending on reaction conditions, have been isolated from these reactions [340–343]. The tetranuclear platinum complex, $[Pt(Arbz\text{-}C,N,S]_4$, has been prepared by the reaction of $Pt(hfac)_2$ with 2-(1-naphthyl)benzothiozoline is refluxing toluene [340]. These molecules comprise of eight-membered ring of alternating M (Pd or Pt) and S atoms. The ligand binds the metal in C,N,S-tridentate fashion [340,342]. Reaction between $[Pd(OAc)_2]_3$ and 1,4-bis(benzothiazol-2-yl)benzene (**50**) in refluxing acetic acid results into double metalated brick-red product, $[Pd_2(\mu\text{-}OAc)_2\{1,4\text{-}(C_6H_4NCS)_2C_6H_4\}]_2$ [344]. Palladation of 1,3-bis(benzimidazol-2-yl)benzene (**51**) with palladium acetate affords an insoluble product which on reaction with TsOH followed by potassium hydroxyacetate in dmso yields a yellow crystalline carboxylato bridged tetranuclear palladium complex [345].



Ar = Ph or 1-napthyl

(49)



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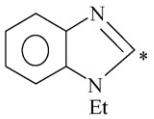
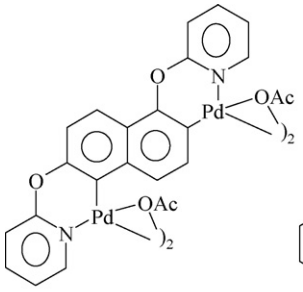
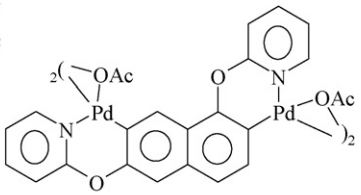


(51)

Double metalation of 1,3- and 1,4-bis(2-pyridyloxy)benzenes and bis(2-pyridyloxy)naphthalenes with palladium acetate affords acetato-bridged tetranuclear palladium complexes [346–348]. Metalation of 1,6-bis(2-pyridyloxy)naphthalene takes place at two different positions depending on reaction conditions. The reaction in acetic acid at room temperature gives 2,5-dipalladated regio isomer (**52**), but under refluxing conditions 2,7-dipalladated isomer (**53**) is obtained [339]. Orthometalation of 1,3-di(2-pyridyl)benzene with $[Pd(OAc)_2]_3$ in acetic acid results into a tetranuclear complex, $[Pd_4(\mu\text{-}OAc)_4(py_2C_6H_2)_2]$ which has an open book structure with dimetalated ligand planes are at an angle of 26.3° [349].

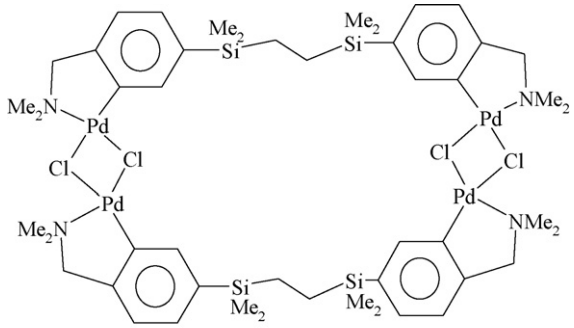


(52)



(53)

van Koten and co-workers [350–352] have studied cyclopalladation of carbosilanes. The reactions of $Pd(OAc)_2$ with carbosilanes in the presence of LiCl afford tetranuclear (**54**) [351] and dendric structures [344]. The reaction of $[Pd\{2\text{-}Me_2NC_6H_4CH(SiMe_3)\}(2\text{-}Me_2NCH_2C_6H_4)]$ with *trans*-$PdCl_2(SEt_2)_2$ in refluxing chloroform or toluene yields alkylidene bridged tetranuclear palladium complex $[Pd_4(\mu\text{-}Cl)_4(\mu\text{-}CHC_6H_4NMe_2\text{-}2)_2(SEt_2)_2]$ [350].



(54)

The reaction of $[PdX(C_6F_5)(NCMe)_2]$ with phenylvinyl sulfide ($PhSCH{=}CH_2$) yields $[Pd(\mu\text{-}X)(PhSCH\text{–}CH_2C_6F_4)]_4$ (X = Cl or Br) in which phenylthiomethyl group acts as a bidentate-bridging ligand holding two "$Pd_2(\mu\text{-}Cl)_2$" units. The four-palladium atoms lie at the corners of a tetrahedron [353]. Metalation of N-arylsufonylglycine ($ArSO_2NHCH_2COOH$, Ar = Ph or 4-MeC_6H_4) with H_2PdCl_4 at pH 3.4 results into a tetranuclear complex, $Na_2[Pd_2Cl_2(Argly\text{-}O,N,C)_2(Argly\text{-}O,O)_2]_2{\cdot}xH_2O$ in which ligand exhibits versatile coordination modes [354].

Unlike nitrogen donor ligands, double metalation of phosphorus donor ligands is rather scanty. Oxidative addition of $Ph_2PC_6H_4Br\text{-}2$ to $Pd(dba)_2$ in toluene leads to the formation of a tetranuclear complex (**55**) [355,356], which in solution, exists in an equilibrium with a mononuclear palladium complex, *cis*- and/or *trans*-$[PdBr(Ph_2PC_6H_4)(PPh_2C_6H_4Br\text{-}2)]$. The bridging bromide can be exchanged by chloride or carboxylate on treatment with Bu_4NCl or AgO_2CR (R = Me, CF_3) [356]. The structure comprises of a parallelogram of four-palladium atoms (Fig. 23) with alternate sides bridged by two halides and two metalated phosphine ligands. The metalated phosphine binds the palladium atom in a head-to-tail fashion. The Pd···Pd distances in the metalated ligands are shorter (~3.08 Å) than the Pd_2X_2 bridge (~3.60 Å) [355,356]. Double metalation of 2-methylresorcinol bis(diphenyl)phosphite has been reported [357]. Insertion of $PdCl_2$ into P(1)–C(1) bond of **56** leads to the formation of a tetranuclear complex (**57**) in which two hinged "$Pd_2(\mu\text{-}Cl)_2$" units are joined together by the two tridentate P_2C donor sets [358].

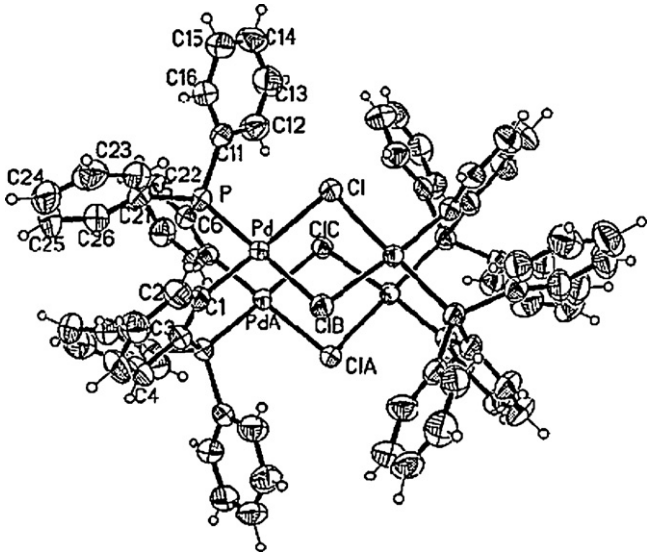
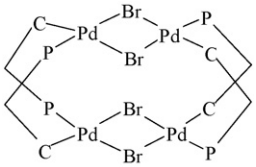
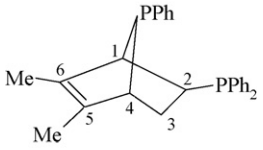


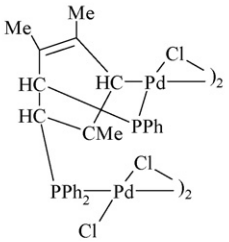
Fig. 23. Structure of $[Pd(\mu\text{-}Cl)\{\mu_2\text{-}(C_6H_4)PPh_2\}]_4$; [356] (Reproduced with permission of American Chemical Society).



(55)



(56)



(57)

4. High-nuclearity complexes

The metal square planes in high-nuclearity complexes can be arranged in many ways, and the number of possible arrangements increases with increasing nuclearity from penta, hexa, hepta to octa.

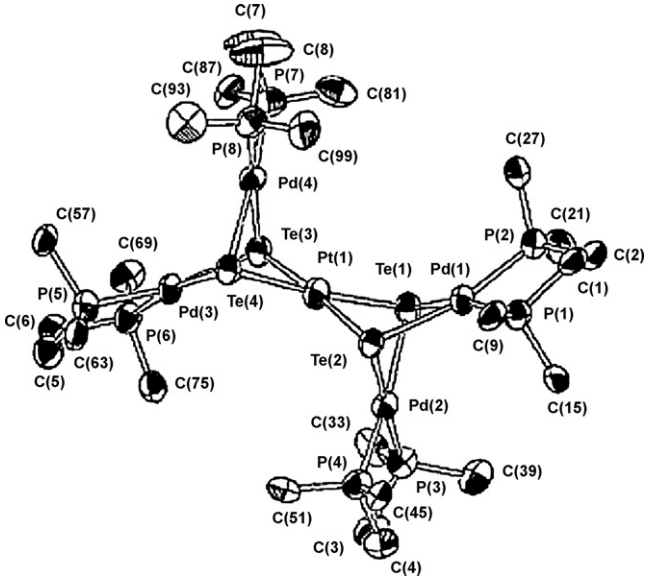
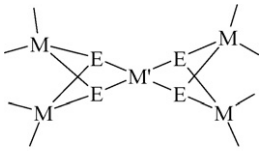


Fig. 24. Molecular structure of $[\{(dppe)_2Pd_2(\mu\text{-}Te)_2\}_2Pt]^{2+}$; [360] (Reproduced with permission of Elsevier Ltd.).

However, only few arrangements have been recognized as the number of fully characterized complexes reported to date are not too many. The high-nuclearity complexes, in general, are derived from chalcogenido and chalcogenolate bridging ligands.

Investigations on pentanuclear complexes are rather limited. The complexes, both homo- and hetero- nuclear, of composition $[\{(PR_3)_4M_2(\mu\text{-}E)_2\}_2M']$ (M = Pd or Pt, M′ = Pd or Pt, E = S, Se, Te), have been synthesized by exploiting outstanding nucleophilicity of "$M_2(\mu\text{-}E)_2$" core ***[42,36,38,359,360]. These complexes have a structure in which central metal square plane is coordinated with four chalcogenido ligands of two hinged binuclear fragments, "$(PR_3)_4M_2(\mu\text{-}E)_2$" (**58**). The ^{31}P NMR spectra display a single resonance indicative of magnetic equivalence of all the phosphorus nuclei [38,359]. Some of these complexes, $[\{(PPh_3)_4Pt_2(\mu\text{-}S)_2\}_2Pd]^{2+}$ [36], $[\{dppe)_2Pd_2(\mu\text{-}Te)_2Pd][BPh_4]_2$ [359] and $[\{(dppe)_2Pd_2(\mu\text{-}Te)_2\}_2Pt][BPh_4]_2$ (Fig. 24) [360] have been structurally characterized (Table 9). The four chalcogenido ions of the two binuclear units bind the central square-planar metal atom. The complex $[\{dppe)_2Pd_2(\mu\text{-}Te)_2\}_2Pd][BPh_4]_2$ undergoes irreversible reduction at −1.84 and −2.44 V and oxidation at −1.32 and −1.00 V [359].



(**58**)

Nucleophilicity of chalcogenido ligands has been exploited to construct hexa nuclear complexes. A variety of reactions have been explored for the synthesis of these complexes. The reactions of bis(trimethylsilyl)chalcogenide, $(Me_3Si)_2E$ (E = S or Se), with palladium(II) precursors have been studied by Fenske et al. [64,361–363], while oxidative addition of chalcoenide ligands on palladium(0) complexes have been investigated by Brennan et al. [364] and Laitinen and co-workers [58,140,365,366]. Reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ with $(Me_3Si)_2Se$ in thf yields a hexanuclear allylpalladium complex, $[Pd_6(\mu\text{-}Se)_3(\eta^3\text{-}C_4H_7)_6]$ consisting of distorted trigonal prismatic geometry (**59**) [362]. The three faces of

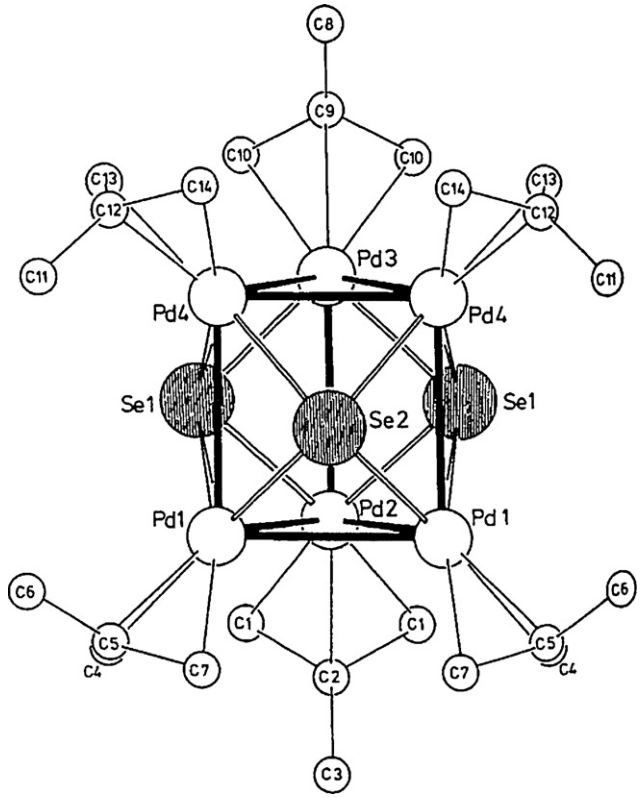
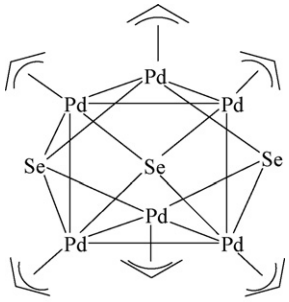


Fig. 25. Molecular structure of $[Pd_6(\mu\text{-}Se)_3(\eta^3\text{-}C_4H_7)_6]$; [362] (Reproduced with permission of Wiley-VCH Verlag GmbH).

the prism are occupied by the bridging selenido ligands (Fig. 25) [362].



(**59**)

The reaction of $[PdCl_2(PPh_3)_2]$ with $(Me_3Si)_2Se$ affords a mixture of multinuclear palladium complexes, $[Pd_3(\mu\text{-}Se)_2(SeSiMe_3)_2(PPh_3)_4]$ (**60**), $[Pd_5(\mu\text{-}Se)_5(PPh_3)_5]$ (**61**) and $[Pd_8(\mu\text{-}Se)_8(PPh_3)_8]$ (Fig. 26) (**62**) [64]. The complex **60** on treatment with $[CpCrCl_2(thf)]$ and $[PdCl_2(PPh_3)_2]$ yields $[Pd_6(\mu\text{-}Se)_4Cl_4(PPh_3)_6]$ (Fig. 27) (**63**), $[Pd_8Se_8Cl(PPh_3)_8]^+[CpCrCl_3]^-$ (**64**), $[Pd_5Se_4Cl(PPh_3)_6]$ (**65**) and $[Pd_7Se_6(SeH)Cl(PPh_3)_7]$ (Fig. 28) (**66**) [64]. The reaction of $[PdCl_2(PPh_3)_2]$ with NaSePh yields $[Pd_3Se(SePh)_3\ (PPh_3)_3]Cl$ and a hexanuclear complex $[Pd_6Cl_2Se_4(SePh)_2(PPh_3)_6]$ (**67**) formed by Se–C bond cleavage [140].

Brennan et al. [364] isolated dark green crystals of a hexanuclear palladium complex, $[Pd_6(\mu\text{-}Te)_6(PEt_3)_8]$ (**68**) in 2% yield from an oxidative addition reaction of $[Pd(PPh_3)_4]$ with PEt_3Te is toluene at room temperature. In addition to **68**, a binuclear complex $[Pd_2(\mu\text{-}Te)_2(PEt_3)_4]$ also formed as dark red crystals in 40% yield. Reactions of $[Pd(PPh_3)_4]$ with R_2Te_2 (R = Ph or 2-thienyl) in dichloromethane affords $[Pd_6(\mu\text{-}Te)_4Cl_2(TeR)_2(PPh_3)_6]$

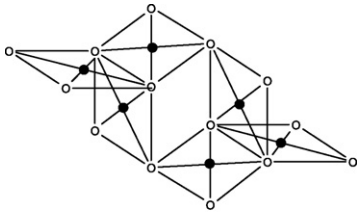
Table 9
X-ray structural characterized penta-, hexa-, hepta- and octa-nuclear complexes.

Complex	Comments	Reference
$[\{(PPh_3)_4Pt_2(\mu\text{-}S)_2\}_2Pd]^{2+}$		[36]
$[\{(dppe)_2Pd_2(\mu\text{-}Te)_2\}_2Pd][BPh_4]_2$	Pd–Te = 2.595 (2)–2.619 (2) Å	[359]
$[\{(dppe)_2Pd_2(\mu\text{-}Te)_2\}_2Pt][BPh_4]_2$	Pd–Te = 2.599 (1)–2.636 (1) Å Pt–Te = 2.598 (1)–2.604 (1) Å	[360]
$[(PPh_3)_6Pd_5(\mu\text{-}Se)_4Cl_2]$	Pd–Se = 2.393 (4)–2.482 (4) Å (μ_3-Se bridging) Pd–Pd = 3.117 (3)–3.323 (3) Å	[64]
$[(PPh_3)_5Pd_5(\mu\text{-}Se)_5]$	Pd–Se = 2.386 (4)–2.638 (4) Å contains μ_2-, μ_3- and μ_5-Se bridges Pd···Pd = 2.943 (4)–3.609 (3) Å	[64]
$[Pd_6(\mu\text{-}Se)_3(\eta^{3-}C_4H_7)_6]$	Pd–Se = 2.411–2.678 (2) Å Pd···Pd = 2.884 (3)–3.149 (2) Å	[362]
$[Pd_6Se_4Cl_4(PPh_3)_6]$		[64]
$[Pd_6Se_4(SeH)_4(PPh_3)_6]$		[64]
$[Pd_6Se_4(SeH)_2Cl_2(PPh_3)_6]$		[64]
$[Pd_6(\mu\text{-}S)_4(\mu\text{-}SH)_2\{S_2P(OEt)_2\}_2(PPh_3)_4]$	Pd–S = 2.310–2.393 Å Pd···Pd = 3.090–3.207 Å	[363]
$[Pd_6(\mu\text{-}Se)_4(\mu\text{-}Cl)_2(SePh)_2(PPh_3)_6]$	Pd–Se = 2.4104 (15)–2.4559 (15) Å	[140]
$[Pd_6(\mu\text{-}Te)_4(\mu\text{-}Cl)_2(TePh)_2(PPh_3)_6]$	Pd–Te = 2.63 (av) Å	[366]
$[Pd_6(\mu\text{-}Te)_4(Te\text{–}Th)_4(PPh_3)_6]$	Pd–Te = 2.6059 (av) Å	[58]
$[Pd_6(\mu\text{-}Te)_4(\mu\text{-}Cl)_2(Te\text{–}Th)_2(PPh_3)_6]$	Pd–Te = 2.5931 (av) Å	[58,365]
$[Pd_6(\mu\text{-}Te)_6(PEt_3)_8]$	Pd–Te = 2.59–2.64Å	[364]
$[Pd_6(\mu\text{-}S_2)_3(\mu\text{-}Cl)_6]$	Trigonal prismatic	[368]
$[Pd(SPr^n)_2]_6$	Orange red needles Pd–S = 2.282–2.450 (2) Å	[373]
$[Pd(SBu)_2]_6$		[374]
$[Pd(SC_{12}H_{25})_2]_6$	Pd–S = 2.32 (av) Å Pd···Pd = 3.11 (av) Å	[378]
$[Pd(SCH_2COOMe)_2]_6$	Pd–S = 2.309 (1)–2.324 (1) Å Pd···Pd = 3.0495 (5)–3.1439 (6) Å	[375]
$[Pd(SeCH_2CH_2CH_2NMe_2)]_6$	Pd–Se = 2.425 (2)–2.451 (2) Å Pd···Pd = 3.1528 (15) Å	[377]
$[Pd(SeCH_2CH_2COOMe_2)_2]_6$		[91]
$[Pd(SCH_2CH_2CH_2S)]_6$	Pd–S = 2.311 (3)–2.338 (3) Å Pd···Pd = 3.050–3.090 Å, S–Pd–S = 79.83–99.73°	[107]
$[Pd\{(S_2C_2(COOMe)_2\}]_6$	Pd–S = 2.2911 (7)–2.3882 (7) Å Pd···$Pd_{(adjacent)}$ = 3.232–3.434 Å	[382]
$[Pt_6(SCH_2CH_2NH_2)_8]Br_4{\cdot}6H_2O)$	Pt–S = 2.30 (2) (av) Å	[385]
$[Pd_6(SCH_2CH_2NH_2)_8][Cl]_4$		[383]
$[Pd_6(SCH_2CH_2NH_2)_8]Br_4{\cdot}6H_2O$	Pd···Pd = 3.1886 (6) Å	[384]
$[Pd_6(SCH_2CH_2NH_2)_8][Pd(NH_2CH_2CH_2OH)_4][Cl]_6{\cdot}5H_2O$	Pd–$S_{(chelate)}$ = 2.274 (av) Å Pd–$S_{(monodenetate)}$ = 2.322 (1) Å	[386]
$[Pd_6(SCH_2CH_2SBz)_8][BF_4]_2$	Pd–S = 2.335 (5) (av) Å for central Pd atoms = 2.304 (4) (av) Å for terminal = 2.322 (4) (av) Å for thioether	[387]
$[\{Pt_3(\mu\text{-}PPh_2)_4(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]$	Pt–P = 2.303 (av) Å Pt–Cl = 2.418 (2), 2.421 (2) Å Pt···Pt = 3.500 (1)–3.610 (1) Å	[388]
β-$[PdCl_2]_6$	Pd–Cl = 2.310 (4) (av) Å Pd–Cl–Pd = 90.70 (5)–92.04 (5)° Pd···Pd = 3.283 (1)–3.329 (2) Å	[394,395]
β-$[PtCl_2]_6$	Pt–Cl = 2.34–2.39 Å Pt···Cl = 3.32–3.40 Å	[399]
$[Pd_7Se_6(SeH)Cl(PPh_3)_7]$		[64]
$[Pd_8(\mu\text{-}Se)_8(PPh_3)_8]$		[64]
$[Pd_8Se_8Cl(PPh_3)_8][CpCrCl_3]$		[64]

Table 9 (*Continued*)

Complex	Comments	Reference
$[Pd_8(SPr^n)_{16}]$	Pd–S = 2.370 (6) (av) Å Pd···Pd ≅ 3.17 (2) Å	[380]
$[Pd_8(\mu\text{-}S_2)_4Cl_8]$	Cube Pd–S = 2.271 (6)–2.285 (5) Å S–S = 2.100 (7)–2.110 (8) Å Pd···Pd = 3.171 (2)–3.420 (5) Å	[367]
$[Pd_6(\mu\text{-}OAc)_8(\mu\text{-}NO)_2]$	Pd_4 distorted tetrahedron; opposite edges of tetrahedron are bonded to two isolated Pd atoms through acetate bridges Pd···Pd = 3.058–2.565 Å	[199]
$[Pt(\mu\text{-}9MeGu)(PMe_3)_2]_6[NO_3]_6\cdot H_2O$	Pt–P = 2.245 (7) Å Pt–N = 2.10(av) Å Cyclic hexamer	[404]
$[Pd_8(\mu\text{-}OAc)_8(\mu\text{-}NO)_8]$	Tetragonal prismatic Pd···Pd = 2.865 (1) Å Pd–N = 1.92 (2) Å Pd–O = 1.99 (av) Å	[406]

(**69**) [58,366]. The complexes, **63** [64], **67** (Fig. 29) [140], **68** [364], **69** [58,366], $[Pd_6Te_4(TePh)_4(PPh_3)_6]$ [58], $[Pd_6Se_4(SeH)_2Cl_2(PPh_3)_6]$ [64] and $[Pd_6Se_4(SeH)_4(PPh_3)_6]$ [64] are isostructural (**70**). In these complexes the two Pd_3E_2 fragments are joined together in a fashion so as to give planar parallelogram comprising of six square-planar palladium atoms.



(70)

The lability of the chloride ligand in $[\{dppp)_2Pt_2(\mu\text{-}S)_2\}PtCl_2]$ has been exploited in evolution of high (hexa- and hepta-) nuclearity platinum complexes, $[\{(dppp)_2Pt_2(\mu\text{-}S)_2\}\{Pt_2(\mu\text{-}S)_2\}]$ and $[\{(dppp)_2Pt_2(\mu\text{-}S)_2\}\{Pt_2(\mu\text{-}S)_2\}PtCl_2]$ [39]. These complexes have been characterized by ESI-MS and NMR (^{31}P and ^{195}Pt) spectroscopy.

Hexa- and octa-nuclear palladium (disulfide) chlorides, $[PdSCl]_n$ (n = 6 or 8) have been prepared by heating palladium metal with S in SCl_2/S_2Cl_2 in a quartz ampoule [367,368]. The hexanuclear complex, $[Pd_6(S_2)_3Cl_6]$ has a trigonal prismatic geometry with three disulfide groups in front of the side faces. The six chloride ligands form μ_2-bridges with each palladium atom [368]. In the octanuclear complex, $[Pd_8(S_2)_4Cl_8]$, palladium atoms form a cube with μ_2-bridging chloride on eight edges. The disulfide groups occupy the front four faces of the cube (Fig. 30) [367].

The methanothermal reaction between Na_2PdCl_4 and Na_2S_4 in the presence of $[MeN(CH_2CH_2)_3NMe]I_2$ in 1:3:1 ratio at 110 °C yields a reddish black hexanuclear complex, $Na_3[MeN(CH_2CH_2)_3N]_3[Pd_6(C_2S_6)(S_3)_6]\cdot 3MeOH$ [369]. The reaction with $PdCl_2$, instead of Na_2PdCl_4, at 80 °C affords another hexanuclear complex having rectangular rod shaped crystals of $Na_2[MeN(CH_2CH_2)_3N)]_4[Pd_6(C_2S_6)(S_3)_4(S_4)_2]\cdot MeOH$. All six palladium atoms in the former lie in the same plane. Each sulfur atom of the $[C_2S_6]^{6-}$ and each S_3^{2-} ligand are coordinated to two different square-planar palladium metal atoms [369].

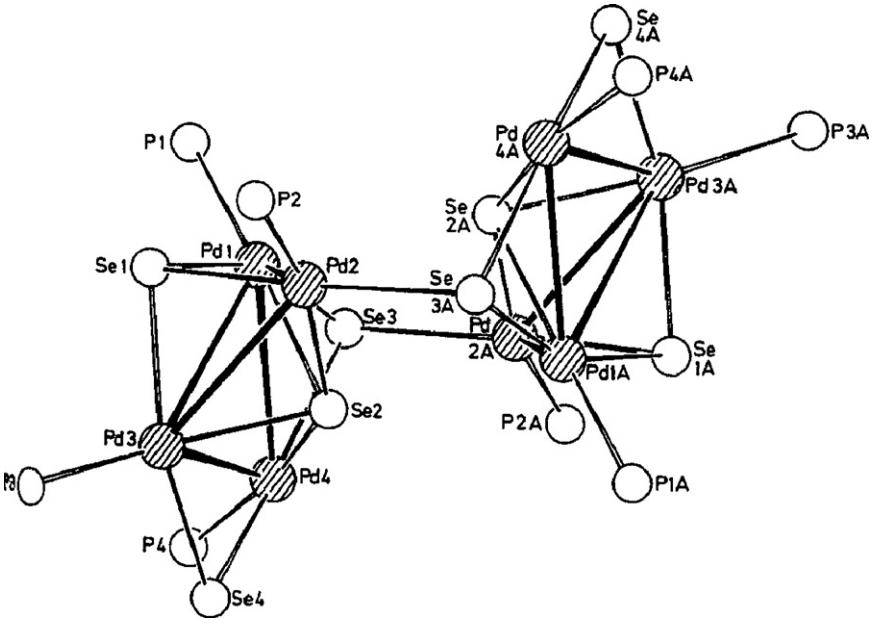


Fig. 26. Molecular structure of $[Pd_8Se_8(PPh_3)_8]$; [64] (Reproduced with permission of Wiley-VCH Verlag GmbH).

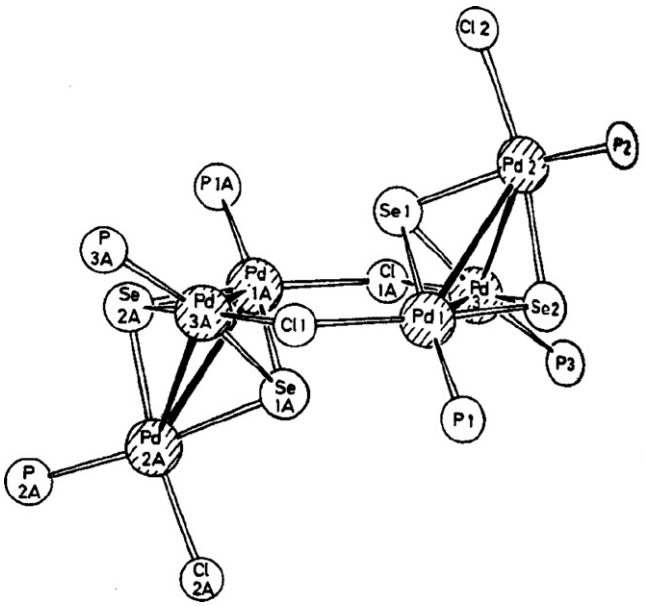


Fig. 27. Molecular structure of $[Pd_6(\mu\text{-}Se)_4(\mu\text{-}Cl)_2Cl_2(PPh_3)_6]$; [64] (Reproduced with permission of Wiley-VCH Verlag GmbH).

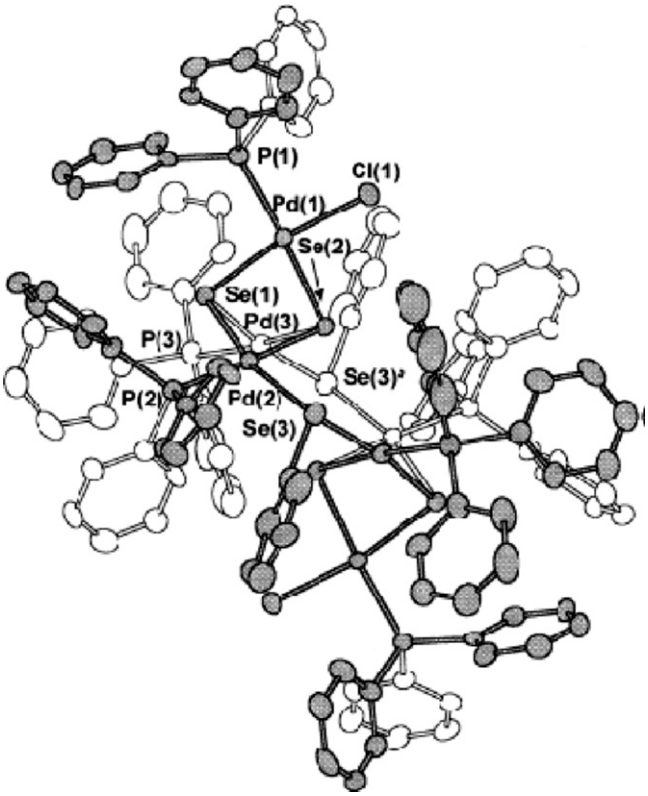


Fig. 29. Molecular structure of $[Pd_6(\mu\text{-}Se)_4Cl_2(SePh)_2(PPh_3)_6]$; [140] (Reproduced with permission of Elsevier Ltd.).

Although homoleptic chalcogenolate complexes of palladium and platinum, $[M(ER)_2]_n$, have been described as insoluble polymeric materials [2–4,370–372], structural characterization has revealed their cyclic hexameric structure. These complexes are readily obtained by the reaction of a metal salt either with free thiol or with the ammonium/sodium salt of organochalcogenolate (Eq. (26)) [91,373–378]. Oxidation of [Pd(pdt)(dppp)] (pdt = propane-1,3-diolate) by oxygen in dmf yields $[Pd(pdt)]_6$ [107]. These complexes have been unambiguously characterized by X-ray single crystal analyses [91,107,373–375,377,378]. DFT calculations on $[Pd(SMe)_2]_n$ ($n = 6$ or 8) have shown that Pd–S_π bonding play a crucial role in stabilizing tiara like structure with $n = 6$ or 8 while structures with different n have poor stability [379]. In these complexes each palladium atom is approximately square planar and is coordinated with four organochalcogenolate ligands. All palladium atoms are linked with each other by bridging chalcogenolate groups (**71**) leading to the formation of hexanuclear cyclic ribbon. As a consequence of the formation of Pd_6E_{12} 'hexagon' (Fig. 31) the E–Pd–E angles around each palladium atom are split into sets of obtuse (~98°, parallel to the ring axis) and sharpened (~82°,

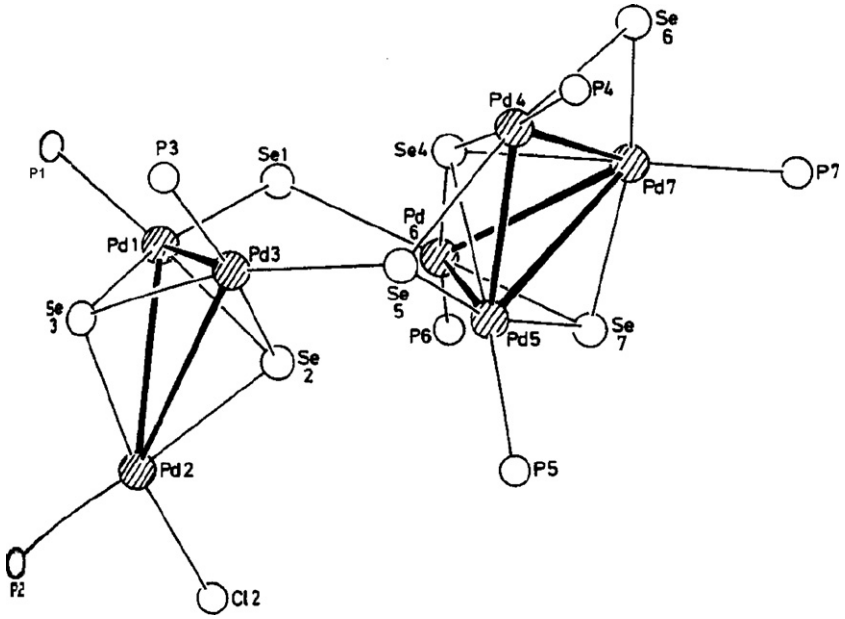


Fig. 28. Molecular structure of $[Pd_7Se_6(SeH)Cl(PPh_3)_7]$; [64] (Reproduced with permission of Wiley-VCH Verlag GmbH).

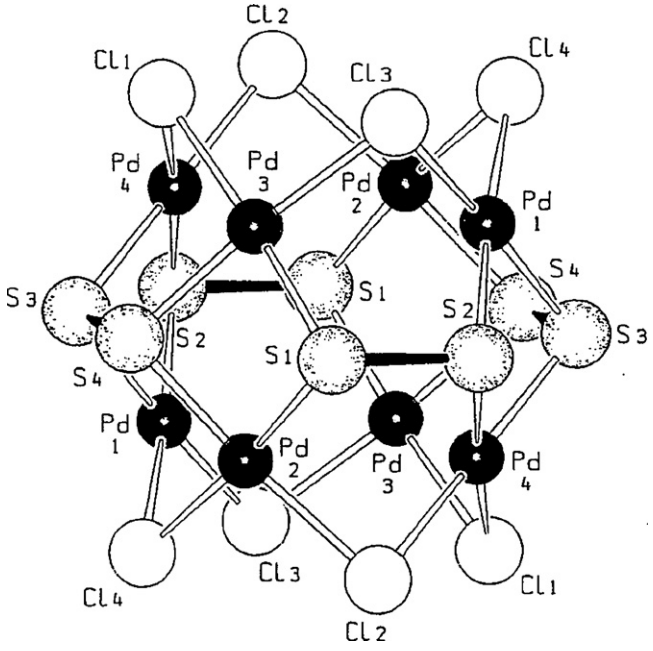


Fig. 30. Molecular structure of $[Pd_8(\mu\text{-}S_2)_4Cl_8]$; [367] (Reproduced with permission of Wiley-VCH Verlag GmbH).

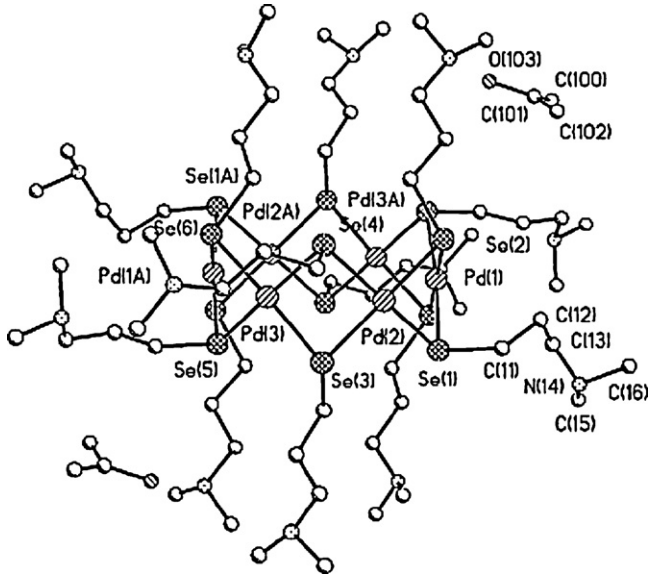
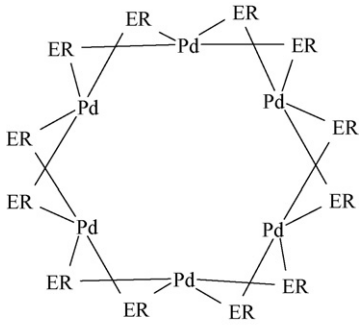


Fig. 31. Structure of $[Pd(SeCH_2CH_2CH_2NMe_2)_2]_6$; [377] (Reproduced with permission of Elsevier Ltd.).

within the ring plane) angles. Recrystallization of $[Pd(SPr^n)_2]_n$ (yellow powder) from pyridine yields two types of crystals, *viz.* light orange prisms (m.p. 154 °C) of $[Pd(SPr^n)_2]_8$ and the dark orange cubes (m.p. 273 °C) of $[Pd(SPr^n)_2]_6$ (**71**) [380]. In the former eight approximately square-planar palladium atoms, each bridged by two SPr^n groups, form a distorted octagonal toroid. The hexamer and octamer exist in equilibrium in solution and the two can readily be interconverted in solution by adding catalytic amount of Li_2PdCl_4 [380].

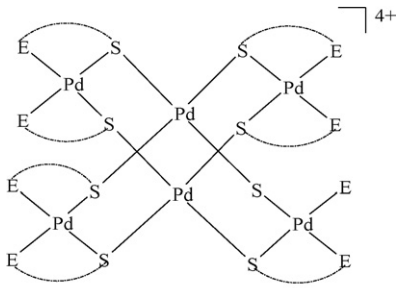


(71)

The complex $[Pd(SeCH_2CH_2CH_2NMe_2)_2]_6$ reacts readily with Na_2PdCl_4 or $[Pd(OAc)_2]_3$ to give binuclear derivatives $[Pd_2(X)_2(SeCH_2CH_2CH_2NMe_2)_2]$ (X = Cl or OAc) [377,381]. Thermolysis of $[Pd(SC_{12}H_{25})_2]_6$ in refluxing (259 °C) diphenylether under argon affords monodispersed palladium sulfide (PdS) nanoparticles of average diameter of 2.87 mm (from TEM) [378]. Pyrolysis of $[Pd_6Te_6(PEt_3)_8]$ at 250 °C yields PdTe [364]:

$$6Na_2PdCl_4 + 12RSH(12NaER) \rightarrow [Pd(ER)_2]_6 + 12HCl\,(12NaCl) \quad (26)$$

Another homoleptic palladium complex $[Pd\{S_2C_2(COOMe)_2\}]_6$ prepared by a transmetallation reaction between $[PdCl_2(MeCN)_2]$ and $[Zn\{S_2C_2(COOMe)_2\}(tmeda)]$, adopt a hexameric structure [382]. The six palladium atoms form a highly symmetric ocatahedral core and the sulfur atoms are centered around this core [382]. Similar octahedral structures have been reported for 2-aminoethanethiolate complexes, $[Pd_6(SCH_2CH_2NH_2)_8][Cl]_4$ [383], $[M_6(SCH_2CH_2NH_2)_8]Br_4{\cdot}6H_2O$ (M = Pd or Pt) [384,385] (**72**) and $[Pd_6(SCH_2CH_2NH_2)_8][Pd(NH_2CH_2CH_2OH)_4]Cl_6{\cdot}5H_2O$ [386]. In the hexanuclear cation of the latter complex, the Pd(2) and Pd(3) atoms have chelated cystamine with the N and S atoms in the *cis* positions. These chelated palladium atoms are joined to each other through Pd(1) which is coordinated by four sulfur atoms [386]. The structure is stabilized by numerous hydrogen bonds. Reactions of $Cp_2Ti(SCH_2CH_2SBz)_2$ with $[Pd(NCMe)_4][BF_4]_2$ leads to the formation of a hexanuclear palladium complex, $[\{Pd(SCH_2CH_2SBz)_2\}_4Pd_2][BF_4]_4$. In this complex four peripheral palladium atoms have chelating thio ether ligands while the two central palladium atoms are each coordinated by four thiolato ligands (**72**) [387].



E^S = $SCH_2CH_2NH_2$; SCH_2CH_2SBz

(72)

Unlike cyclic structures adopted by chalcogenolato bridged complexes, the phosphido-bridged derivatives are isolated in the linear form. The reactions of trinuclear complex, $[Pt_3(\mu\text{-}PPh_2)_4(C_6F_5)_4]^{2-}$ with aqueous HCl yields a hexanuclear complex, $[\{Pt_3(\mu\text{-}PPh_2)_4(C_6F_5)_2\}_2(\mu\text{-}Cl)_2]^{2-}$ formed via an intermediate trinuclear complex, $[Pt_3(\mu\text{-}PPh_2)_4(C_6F_5)_2Cl_2]^{2-}$ (Eq. (27)) [388]. The molecular structure revealed that all the six square-

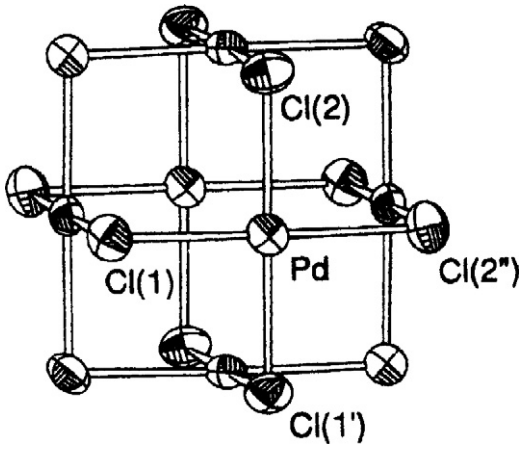
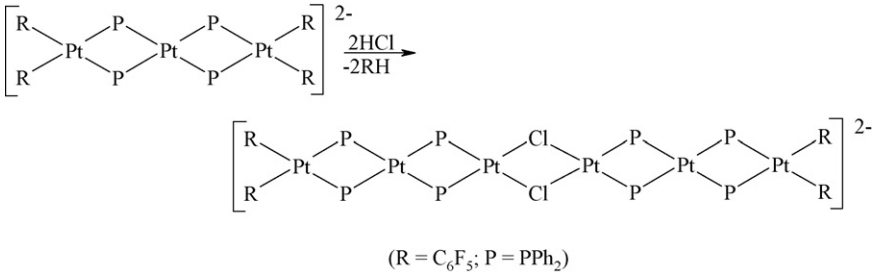


Fig. 32. Structure of β-$[PdCl_2]_6$; [394] (Reproduced with permission of Wiley-VCH Verlag GmbH).

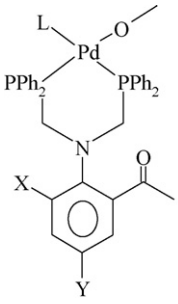
planar platinum atoms are disposed in an almost linear fashion.



(27)

The binary compounds, MX_2 (M = Pd or Pt, X = Cl, Br, I), routinely used as precursors in palladium and platinum chemistry, have halogen bridged structures in the solid state as revealed by various spectroscopic techniques [389–392]. Three polymorphic forms of palladium dichloride have been reported. The structure of commercial $PdCl_2$, which is insoluble in aromatic solvents, is still uncertain. The α-form with an orthorhombic cell (a = 3.81, b = 3.34 and c = 11.0 Å) consists of infinite linear chain of chloride bridged palladium atoms (Pd–Cl = 2.31 Å) [393]. The β-phase consist of discrete hexameric molecules of $[PdCl_2]_6$ [392,394,395]. The molecule has an octahedral array of six square-planar palladium atoms. Each metal atom is coordinated with four bridging chloride ligands which lie at the edges of the octahedron (Fig. 32). The β-phase can be prepared in several ways which include (i) reaction of $[Pd(OAc)_2]_3$ with CO in acetic acid in the presence of perchloric acid [391], (ii) slow decarbonylation of $[Pd_2(\mu\text{-}Cl_2)Cl_2(CO)_2]$ in thionylchloride [394], and (iii) slow recrystallization of $[PdCl_2(PhCN)_2]$ in benzene–chloroform mixture [395]. Recrystallization of β-$PdCl_2$ from aromatic hydrocarbons (*e.g.*, benzene, mesitylene, naphthalene, *etc.*) results into deep-red crystals in which aromatic solvent is co-crystallized with the cubic $[PdCl_2]_6$ giving a layered structure. Each arene molecule makes face-to-face contact with $[PdCl_2]_6$ cluster [395–397]. The platinum chloride, $[PtCl_2]_6$ [398–401], has a structure similar to β-$[PdCl_2]_6$.

Hexanuclear palladium complexes with other ligands have been reported [200,402,403]. In complex **73**, prepared using P_2O-tetradenate ligands, all the six square-planar palladium atoms coordinate with a chelating diphosphine, bridging carboxylate and a halide ligand, so as to give a 48-membered ring with an outer diameter of about 2.5 nm [403].



X	Y	L
OMe	H	Cl
OH	H	Cl
H	OH	Cl
OMe	H	I

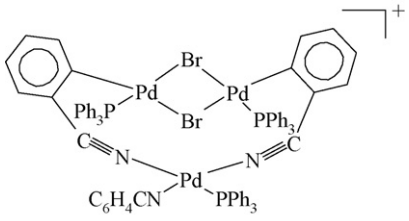
(73)

Treatment of *cis*-$[Pt(NO_3)_2(PMe_3)_2]$ or $[Pt_2(\mu\text{-}OH)_2(NO_3)_2(PMe_3)_2]$ with 9-methylguanine (9-MeGuH) in 1:1/1:2 ratio results into the formation of a colorless hexanuclear complex, $[Pt(\mu\text{-}9MeGu)(PMe_3)_2]_6[NO_3]_6{\cdot}18H_2O$. The molecule comprises of six *cis*-"$Pt(PMe_3)_2$" fragments which are bridged symmetrically by N(1)-deprotonated 9-methylguanine ligands coordinated through N(1) and N(7) atoms [404]. The 9-methylguanine ligands alternatively lie above and below the square planes of platinum atoms. The orthometallated chloro-bridged palladium complex $[Pd_2(\mu\text{-}Cl_2)_2(Me_2NCH_2\text{–}Fc)_2]$ when treated with parabanic acid yields a hexanuclear palladium complex in which palladium atoms define a tapering, twisted trigonal prism [405].

An octa-nuclear palladium complex, $[Pd_8(OAc)_8(NO)_8]$ has been prepared by dissolving palladium nitrate in a mixture of acetic acid–nitric acid. The molecule has a tetragonal prismatic geometry with palladium atoms at the vertices. Each palladium atom is bridged by a pair of acetate groups in *cis* orientation and NO which lie along the horizontal edges of the prism [406].

5. Other tri- and high-nuclearity complexes

Reaction of $[(2\text{-}CNC_6H_4)Pd(\mu\text{-}Br)(PPh_3)]_2$ with Tl(OTf) yields an unusual cyano-bridged cationic complex (**74**) $[Pd_2(\mu\text{-}Br)_2(PPh_3)_2(C_6H_4C{\equiv}N)_2Pd(PPh_3)(C_6H_4CN)]$ [OTf] [407]. Reactions of 1-thia-4,7-diazacyclononane with palladium chloride gives a trinuclear centrosymmetric cation, $[Pd_3L_4Cl_2]Cl_4{\cdot}2H_2O$ [408].



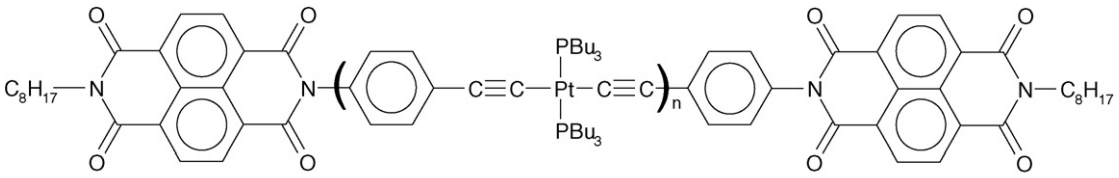
(74)

Acetylide-bridged oilgomeric complexes, $[(PR_3)_2Pt\text{–}C{\equiv}C\text{–}Ar\text{–}C{\equiv}C\text{–}]_n$ and **75**, have been synthesized as platinum centers

Table 10
Reviews on dendrimers and self-assembled molecules dealing with palladium(II) and platinum(II) complexes.

Title	Authors	Reference
Structural aspects of Pt complexes containing model nucleobases	Lippert et al.	[416]
Molecular architecture with metal ions, nucleobases and other heterocycles	Navarro and Lippert	[417]
Self-assembly, symmetry, and molecular architecture: coordination as the motif in the rational design of supramolecular metallacyclic polygons and polyhedral	Stang and Olenyuk	[418]
Molecular architecture of cyclic nanostructures: use of coordination chemistry in the building of supearmolecules with predefined geometric shapes	Stang et al.	[419]
Self-assembly of discrete cyclic nanostructures mediated by transition metals	Stang et al.	[420]
High symmetry coordination cages via self-assembly	Seidel and Stang	[421]
Transition metal-directed assembly of well-defined organic architectures possessing large voids: from macrocycles to [2]catenanes	Fujita and Ogura	[422]
Self-assembling [2]catenanes: molecular magic rings	Fujita	[423]
Metal-directed self-assembly of two- and three-dimensional synthetic receptors	Fujita	[424]
Self-assembly of [2]catenanes containing metals in their backbones	Fujita	[425]
Molecular self-assemblies through coordination: macrocycles, catenanes, cages and tubes	Biradha and Fujita	[426]
Molecular paneling via coordination	Funita et al.	[427]
Multicomponent metal-ligand self-assembly	Fujita et al.	[428]
Coordination assemblies from a Pd(II) cornered square complex	Fujta et al.	[429]
Direct observation of crystalline-state guest exchange in coordination networks	Kawano and Fujita	[430]
Formation of artificial receptors by metal-templated self-assembly	Linton and Hamilton	[431]
Transition metals on structural components in the construction of molecular containers	Jones	[432]
Molecular tectonics: from simple tectons to complex molecular networks	Hosseini	[433]
Metallasupramolecular architectures, an overview of functional properties and applications	van Koten et al.	[434]

influence the π-conjugated electronic system, thereby their photophysical properties [409–412]. Introduction of platinum in these conjugated systems results in efficient production of long-lived triplet excitons by effectively mixing singlet and triplet states. Similarly, trinuclear linear complexes based on other than acetylide ligands have been isolated [413–415].



n = 3, 4, 6, 8, 10

(75)

6. Dendrimers and self-assembled molecules

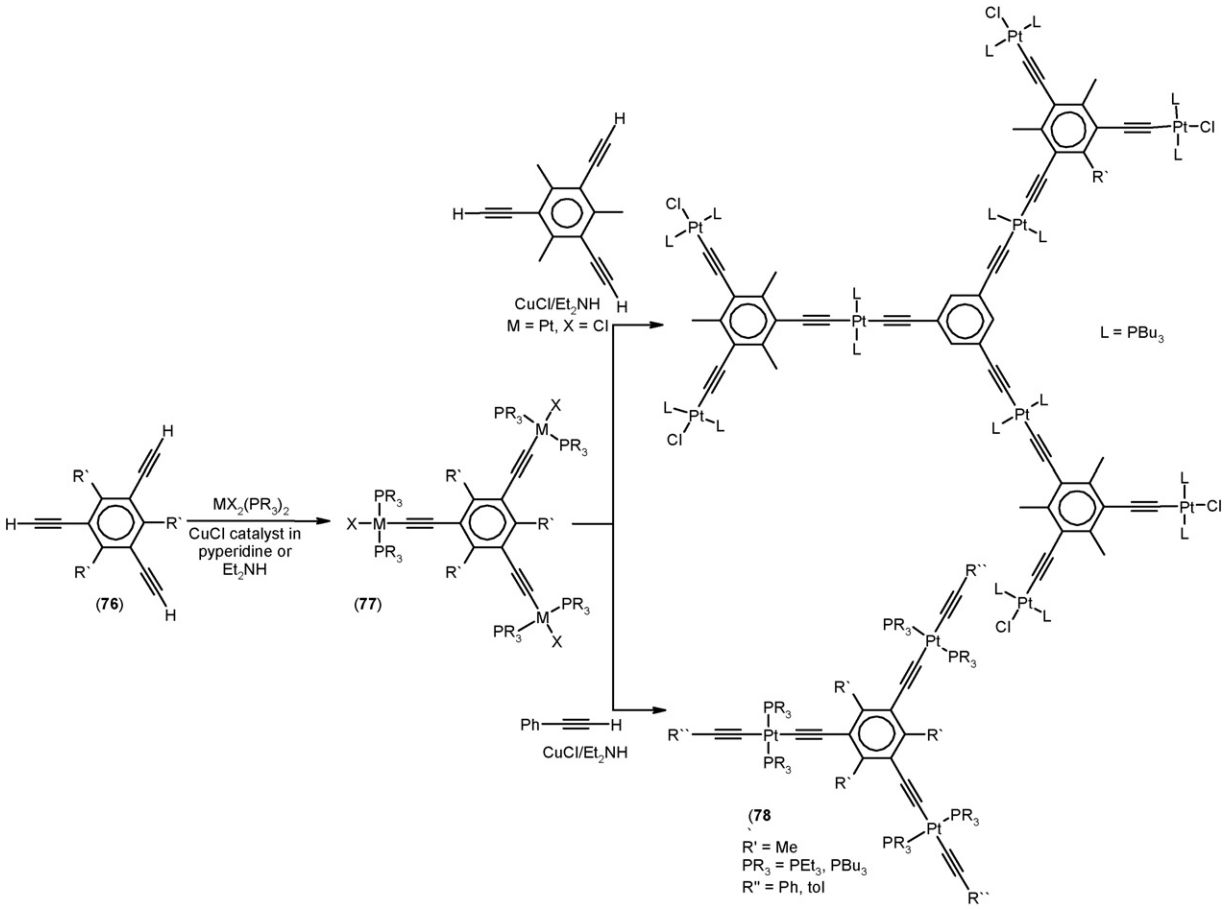
Dendrimers and self-assembled molecules are another family of tri- and high-nuclearity palladium(II) and platinum(II) complexes. The chemistry of these complexes has evolved in the last 15–20 years. The research groups of Lippert [416,417], Stang [418–421], Fujita [422–430] and others [431–434] have made pioneer contributions to the growth and development of the chemistry of these complexes. The progress of work in this area has been reviewed time to time (Table 10). Thus to complement the present review, illustrative examples of these complexes are discussed in this section.

6.1. Dendrimers

Although the chemistry of organic dendrimers has been extensively investigated and reviewed [435], metal dendrimers have attracted attention only recently. The interest in such molecules stems from their possible applications as recoverable and renewable homogeneous catalysts having several active metal centers and also for their redox, liquid crystalline and photophysical properties. A variety of palladium and platinum containing dendrimers have been synthesized by employing convergent (construction from outside to the core) and divergent (growth from the core to outward) strategies and characterized by various spectroscopic methods and X-ray crystallography.

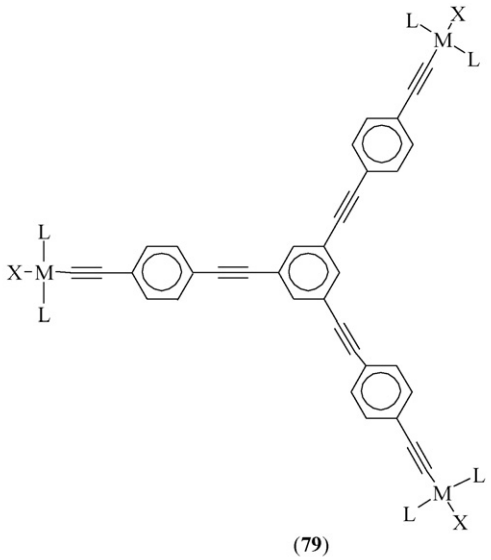
Triethynylbenzenes (**76**) (Scheme 13) based dendrimers of palladium(II) and platinum(II) have been prepared and structurally characterized. Trinuclear acetylide derivatives (**77**) are in general obtained by treatment of 1,3,5-triethynylbenzenes with $MCl_2(PR_3)_2$ (M = Pd or Pt; PR_3 = PEt_3 or PBu_3) in the presence of CuCl as catalyst in refluxing piperidine or diethylamine (Scheme 13) [436–442]. The terminal chloride on each metal atom in **77** can be substituted by other groups including parent alkynyl ligands so as to yield high-nuclearity dendrimers [438]. Higher generation of dendrimes can be and have been grown in stepwise manner by convergent synthesis around **77** as the core [443]. The platinum acetylide dendrimers containing as many as 45 platinum atoms in a molecule have been synthesized [444]. Butadiynyl bridged molecule squares, $[Pt_4(C{\equiv}C{-}C{\equiv}C)_4(L_4)]$ (L = 2 PEt_3, dppp, dcpe) have also been synthesized and structurally characterized [445–447].

Photophysical properties of some of these dendrimers (**77** and **79**) have been investigated [441,442,448,449]. Electronic spectra of free alkynyl ligands and their palladium and platinum complexes display similar absorption bands with comparable extinction coefficients. As there is a slight red-shift of absorption energies from palladium complexes to the corresponding platinum derivatives, the low energy (330–370 nm) absorption band has been attributed to an admixture of $\pi{-}\pi^*$ (C≡CR) (IL)/$d\pi_{(M)} \rightarrow \pi^*$ (C≡C) MLCT transition with predominance of IL character [442,449]. These complexes on photoexcitation at $\lambda > 350$ nm show structured emission



Scheme 13.

bands (515–550 nm) [442,448,449]. The large Stokes shifts with lifetimes of luminescence in microseconds have been ascribed to triplet parentage.

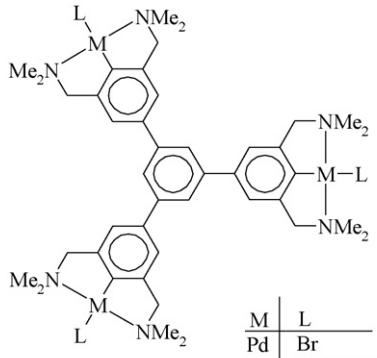


(79)

M = Pd or Pt, L = PEt_3

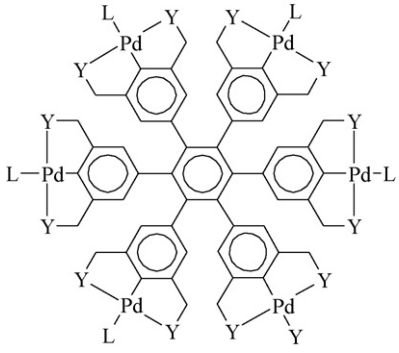
X= Cl, —≡—R (R = p-tol, napthyl, Ph, 2-thienyl, C_6H_4—≡—$SiMe_3$)

van Koten and co-workers [450–453] have employed pincer ligands for the synthesis of palladium and platinum containing dendrimers. Other groups [454,455] have utilized multidentate phosphine ligands in such preparations. Metalation of 1,3,5-tris(pincer) and hexakis(pincer) benzenes afford tri- (**80**) hexanuclear (**81**) dendrimers [451,452]. The latter represents cartwheel type molecules with the spatial arrangements of the metal centers as six-spokes. Multidentate phosphines have been employed to prepare cationic (*e.g.*, **82**, **83**) and neutral (**84**) dendrimers [454–458]. The former shows Pt···Pt interactions in the solid state and are emissive both in the solid state and in solution [454]. The ^{195}Pt NMR spectra display two doublets at around −3847 and −3970 ppm for the central and the terminal platinum atoms with ^{1}J(Pt···P) of ∼4100 Hz [454]. The complex **83** (R = R′ = H) shows polymorphism and crystal form depends on the counter anion as well as conditions of crystallization. For instance, the ClO_4 salt crystallizes in four different forms with colors ranging from yellow–orange–red [454]. The reaction of 1,3,5-tris(di-2-pyridylamino)benzene with palladium chloride or acetate produces triply cyclopalladated complex [459]. Reaction of 1,3,5-triiodomesitylene with $Pd(dba)_2$/$Pd_2(dba)_3$ in the presence of bipy in toluene yields a trinuclear complex, [{PdI(bipy)}$_3$(μ-C_6Me_3)] [460]. The reaction of palladium acetate with 1,3-bis(1-methylbenzimidazol-2-yl)benzene (mbzimph) in acetic acid yields a trimeric orthometalated product [Pd(OAc)(mbzimp)]$_3$ in 88% yield. The cup-shaped trimer possesses a hydrophobic cavity [461].



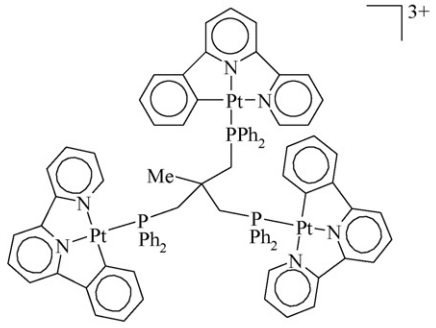
M	L
Pd	Br
Pd	$H_2O(BF_4)$
Pt	Br

(**80**)

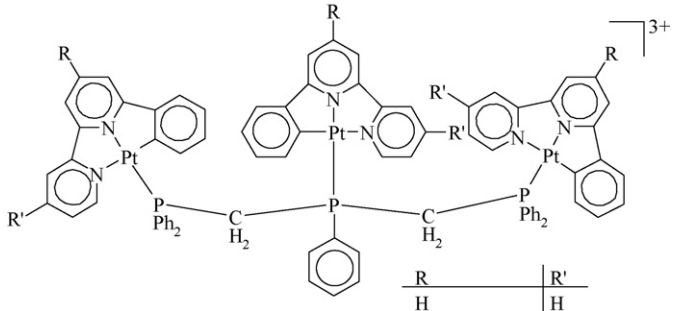


Y	L
SPh	Cl
PPh_2	Cl
pz	OAc
pz	Cl
pz	$H_2O(BF_4)$

(**81**)

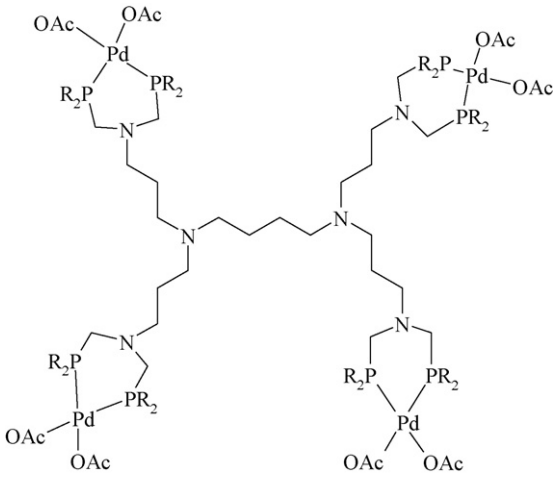


(**82**)



R	R'
H	H
Bu^t	Bu^t
C_6H_4OMe-4	H
EtOOC	H
aza-15-c-5	H

(**83**)

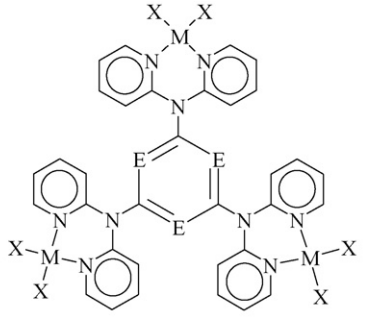


(**84**)

R = Bu^t, c-Hx

The trinuclear complex **80** (M = Pd; L = $H_2O(BF_4)$) shows similar catalytic activity to that of its mononuclear counterpart in double Michael reaction between ethyl α-cycnoacetate and methylvinyl ketone [452,453]. The complexes **84** and their second and third generation dendrimers have been employed in copper free Sonogashira C–C coupling reactions. The third generation dendrimers give lower activity than the **84** and has been attributed to increasing steric bulk around the active metal centers [455].

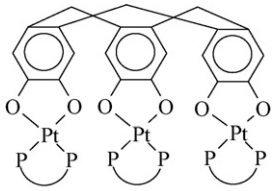
Several starburst ligands such as 1,3,5-tris(7-azaindol-1-yl)benzene (tabH) [462], hexakis (pyrazol-1-yl)benzene [463] and compounds containing di-2-pyridylamino group [459,464–468] have been employed to prepare trinuclear dendrimers. Relative orientation of pyridyl groups on each di-2-pyridylamino unit in the latter (**85**) results into bowl (*e.g.*, [{$PdCl_2$}$_3$(tdab)]), pinwheel (*e.g.*, [{$Pd(OAc)_2$}$_3$(tdab)] and cage shape molecules. The complex [$Pd_3(tab)_2Cl_4$] shows an orange emission at λ_{max} 575 nm at 77 K, but non-emissive at room temperature [462]. Reaction of [$Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$] with 1,3,5-triazine affords a trinuclear complex, [{$PtCl_2(PEt_3)$}$_3$(triazine)], in which structural parameters of triazine does not change significantly on coordination [469]. A pentanuclear palladium complex, [$(PdCl_2)_4py_8$TpyzpzPd] (py_8TpyzpzH$_2$-tetrakis{2,3-(5,6-di-2-pyridylpyrazino)porphyrazine)}) has been isolated. The four $PdCl_2$ units coordinate to the peripheral pyridine nitrogen atoms [470].



(**85**)

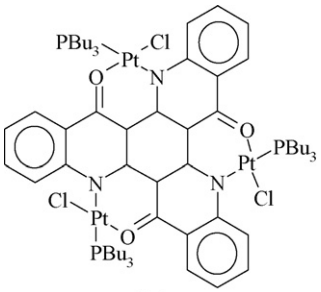
E = CH (1,3,5-tris(di-2-pyridylamino)benzene (tdab)
N (2,4,6-tris(di-2-pyridylamino) 1,3,5-triazine (tdat)
MX_2 = $PdCl_2$, $Pd(OAc)_2$, $PtCl_2$, $PtPh_2$

Macrocyclic host molecules with a shallow molecular cavity, such as cyclotriveratrylene (CTV), cyclotricatechylene (CTC), thiacalixarenes, have been employed for convergent binding of fragments to isolate dendrimers with different nuclearity [471–473]. Thus the reaction of cyclotricatechylene with $PdCl_2L$ (L = 1,2-bis(diphenylphosphino)benzene (dppb), diphenylphosphinoferrocene in methanol/K_2CO_3 yields a bowl shaped trinuclear complex (**86**) [471].



(**86**)

Reaction of $[Et_4N]_2[PdCl_4]$ with tris-(2-hydoxybenzylidene) triaminoguanidine ($[LH_6Cl]$) in the presence of a base (Et_4NOH) in acetonitrile affords dark red crystals of a propeller-like trinuclear complex $[LPd_3Cl_3]^{2-}$ [474]. The reaction of tris(5-bromo-2-hydroxylbenzyl)triaminoguanidinium chloride, $[H_6Br_3L]Cl$, with $PdCl_2$ and sodium 5,5-diethylbarbiturate (Nabar) yields red plates of $[Et_3HN]_6[Et_4N]_6[\{Pd_3(Br_3L)\}_6(\mu\text{-bar})_9]$ containing 18-palladium atoms bridged by barbiturate dianion [475]. The reaction between $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ and trisodium salt of triquinolobenzene yields a trinuclear complex (**87**) in which three platinum atoms are in *syn* positions [476].



(**87**)

6.2. Self-assembled molecules

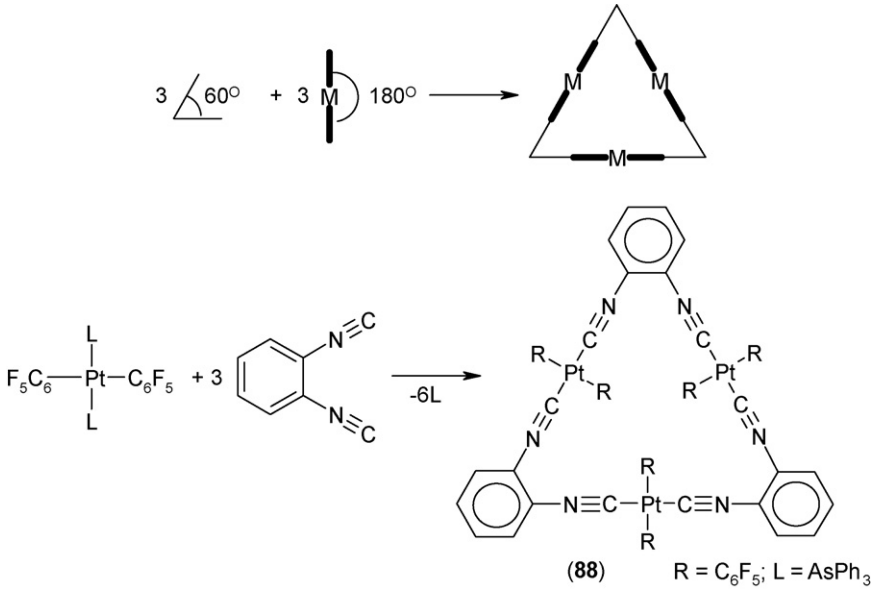
These complexes in general are obtained through design employing a strategy where electron deficient metal centers are spontaneously combined with ligands having donor atoms incapable of forming chelates. Thus a myriad of regularly shaped self-assembled molecules have been isolated by substituting labile ligands in mononuclear palladium and platinum precursors by appropriate organic electron donor ligands. Both *cis*- and *trans*-, amine/phosphine complexes, such as $[M(en)(NO_3)_2]$, $[PtL_2(OTf)_2]$ (L_2 = 2 PR_3 or chelating phosphine), have been successfully used. A variety of multidentate N-donor ligands with varied shapes and sizes as well as biologically relevant molecules (*e.g.*, nucleo bases and heterocyclic model ligands) have been used for designing a wide range of self-assembled 2D and 3D molecules.

6.2.1. Two-dimensional self-assembled molecules

6.2.1.1. Triangular shaped molecules. Molecular triangles represent the simplest monocyclic supera-molecular assemblies. They can, in principle, be built by combination of three non-chelating bridging ligands with three metal centers in one of the following ways:

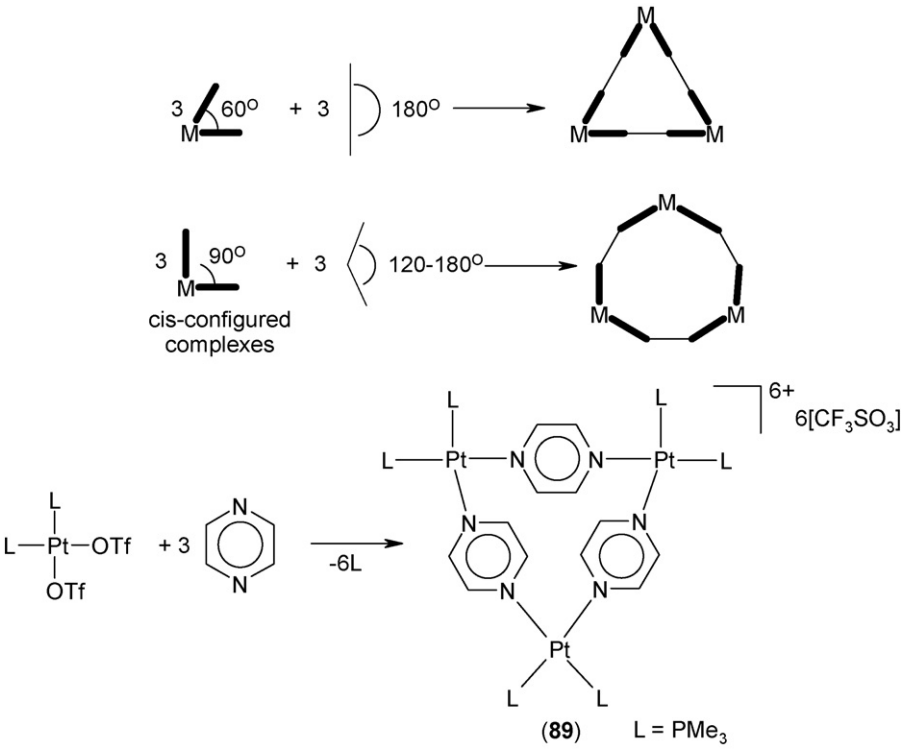
(i) Combination of three linear metal centers (*trans*-configured complexes) with three bidentate ligands with 60° bite angles can produce triangular shaped molecules [477–481]. For example, reaction of *trans*-$[Pt(C_6F_5)_2(AsPh_3)_2]$ with 1,2-phyenlene diisocyanide in dichloromethane at room temperature affords a triangular complex, $[Pt(C_6F_5)_2\{\mu\text{-}C_6H_4(NC)_2\}]_3$ (**88**) in which platinum atoms are at the centers of each side of an equilateral triangle (Scheme 14) [480].

(ii) Combination of the metal centers either with 60° or 90° bond angles with linear (180°) or non-linear (150°) bridging ligands. The majority of the complexes belong to this family of trinuclear self-assembled molecules. Metal fragments in general offer two *cis* coordination sites and occupy the vertices of the triangle (Scheme 15). Thus metal centers bearing chelating ligands, such as en [482–485], tmeda [486,487], substituted bipyridines [488,489], metalated 2-(2-thienyl)pyridine [490], dppf [491] and monodentate ligands like NH_3 [492–494] or tertiary phosphines [495–500] in *cis* positions have been employed. Various neutral nitrogen donor ligands, such as pyrazine [497],

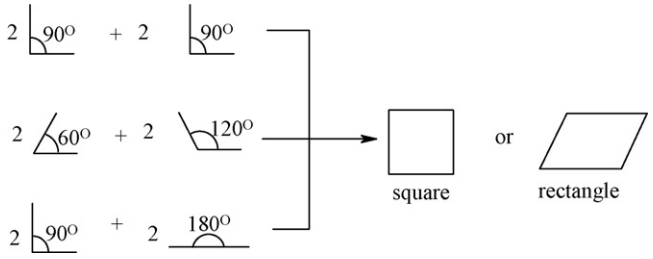


(**88**)

Scheme 14.



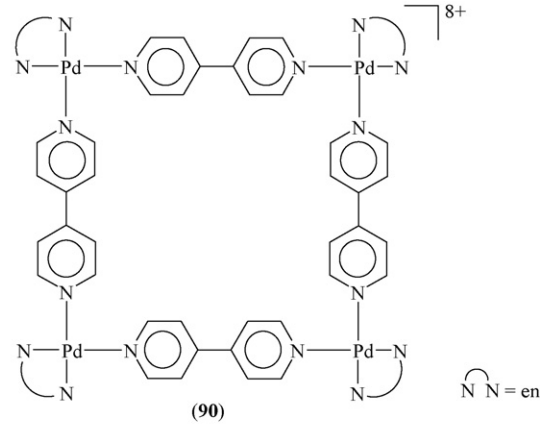
Scheme 15.

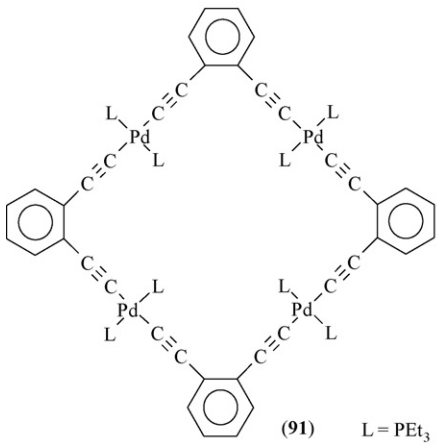


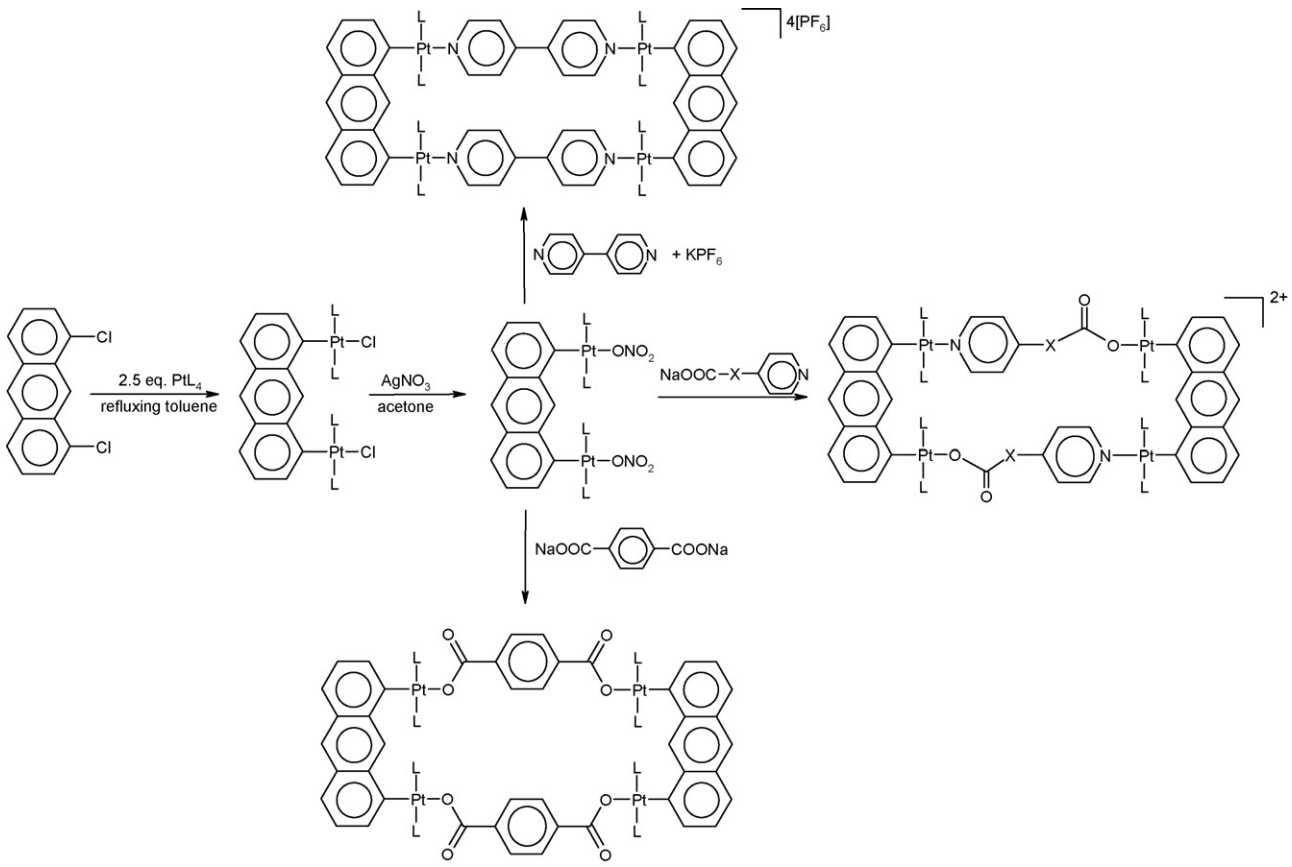
Scheme 16.

2,2′-bipyrazine [482,483], 4,4′-bipyridine, 4,7-phenanthroline [501], bis-pyridines [488], *etc*., diphenylphosphinoacetylene [502] and anionic ligands like nicotinic acid [491], 5-pyrimidine carboxylate [491], 4-(pyrimidene) [489], benzimidazolate [490], phenylenedicarbonylbis(thiourea) [503] and several nucleobases [486,487,492–495,499,500] have been successfully used as bridging ligands for the fabrication of trimetallic complexes. By appropriate choice of ligands cationic and neutral complexes have been isolated. For instance reaction between *cis*-[$Pt(OTf)_2(PMe_3)_2$] and pyrazine in nitromethane yields a pyrazine bridged trinuclear complex **89** [497].

6.2.1.2. Square and rectangular shaped molecules. Combination of four angular ligands with four linear metal centers or vice versa can lead to squares. Alternatively, two different angular subunits can also be used as building blocks (Scheme 16). Both *cis*- and *trans*-"ML_2" ($L_2 = 2PR_3$; P∩P = dppf, dppp) [504–519], $PdCl_2$ [520] and chelating amine fragments "(N∩N)M" (N∩N = en and other chelating amines) [521–527] have been used as tectons for building square and rectangular shaped supramolecules. Various anionic, dianionic and neutral non-chelating bidentate ligands have been used as bridging ligands to yield ionic and neutral complexes (Scheme 17) [504–528]. The en complex (**90**) with 4,4′-bipyridine is readily prepared by treatment of [$Pd(en)(NO_3)_2$] with 4,4-bipyridine in methanol in the presence of bulky anion (ClO_4^-, PF_6^-, NO_3^-). Reaction of $PdCl_2(PEt_3)_2$ with *o*-diethynylbenzene in the presence of CuCl catalyst in diethylamine affords a neutral tetranuclear complex (**91**) [504].



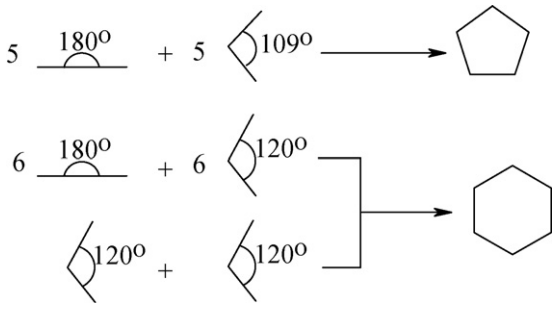




Scheme 17.

6.2.1.3. Pentagonal and hexagonal molecules. Pentagonal and hexagonal self-assembled molecules have been built by combination of five liner (180°) units with five angular (109.5°) components and six linear (180°) subunits with six angular (120°) fragments, respectively (Scheme 18). The hexagons can also be fabricated by employing two different types of angular building blocks.

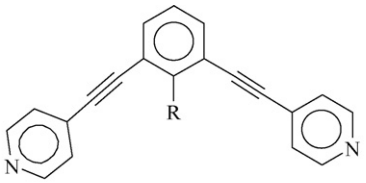
Pentanuclear platinum complexes, $[Pt_5(dpk)_2(dpkOH_2)_3(L)_3]^{4+}$ (**92**) (dpk = 2,2′-dipyridylketone; L = uracil or thymine), have been isolated by treatment of $[Pt(dpk)(H_2O)]^{2+}$ with a nucleobase in the presence of a bulky anion (ClO_4^-, BF_4^- or PF_6^-] [529]. Hexanuclear complexes have been isolated by using nucleobases (*e.g.*, guanosine 5-monophosphate) [530] and neutral donor bridging ligands [478,531–533]. Thus the reaction of *cis*, *trans*-1,3,5-triaminocyclohexane hydrochloride with 1.5 equivalents of $PdCl_2$ yields a hexanuclear complex, $[Pd_6(L)_6Cl_6]^{6+}$ (**93**) (L = 1,3,5-triaminocyclohexane) [471]. A hexanuclear dicarbene complex of platinum, $[Pt(CN)(C_{10}H_{21}N_4)]_6$ (**94**), has been isolated by refluxing an aqueous solution of K_2PtCl_4 containing *tert*-butylisocyanide and hydrazine hydrate [534]. The complex is emissive both in the solid state and in solution.



Scheme 18.

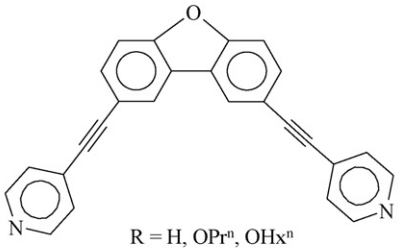
6.2.2. Three-dimensional self-assembled molecules

Unlike designing 2D self-assembled molecules, construction of three-dimensional (3D) compounds is more complex as it involves combination of many more building blocks in which at least one of the blocks is a multidentate ligand capable of holding more than two metal atoms. In general bidentate-bridging ligands (*e.g.*, **95**–**97**) and square-planar metal atoms assemble in closed M_nL_{2n} coordination 3D polyhedra with n often having magic number value (n = 6, 12, 24, 60). Thus with suitable bent bridging ligands, self-assembled 3D molecular polyhedra, such as tetrahedron, octahedron, box [535], cube [536], sphere [537], triangular prism [538], tube [539] and cage [540–547], have been isolated and characterized. Multidentate ligands like 2,4,6-tri(4-pyridyl)-1,3,5-triazine (**98**) [541,542], 2,4,6-tri(3-pyridyl)-1,3,5-triazine (**99**) [543], 1-(5-pyrimidine)-3,5-bis(3-pyridyl)benzene (**100**) [544] and other heterocyclic nitrogen donor ligands [545–548], have been used extensively to design molecular cages. The nano-size cavity (~2 nm) of the molecular cage in $[M_6L_4]^{12+}$ (L = **98**) (**101**) accommodate a variety of guest molecules to give host–guest complexes [549,550]. Other polyhedra also encapsulate various anions (NO_3^-, PF_6^-, *etc.*) and organic molecules [551]. The cage molecules have been used for cavity directed synthesis, *e.g.*, oligomerization of trialkoxysilanes [552], photoinduced oxidation of alkanes [553], and spin–spin interactions between encapsulated organic radicals [554].



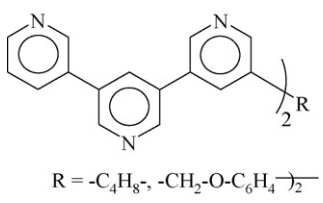
R = H, OPr^n, OHx^n

(**95**)



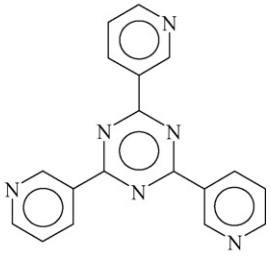
R = H, OPr^n, OHx^n

(**96**)

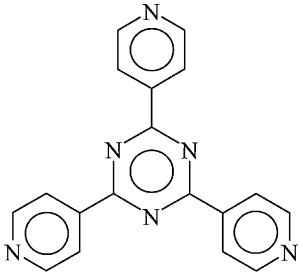


R = -C_4H_8-, -CH_2-O-C_6H_4-)$_2$

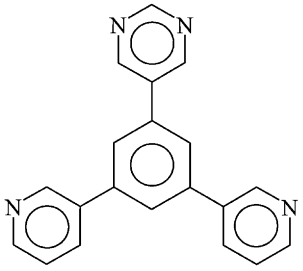
(**97**)



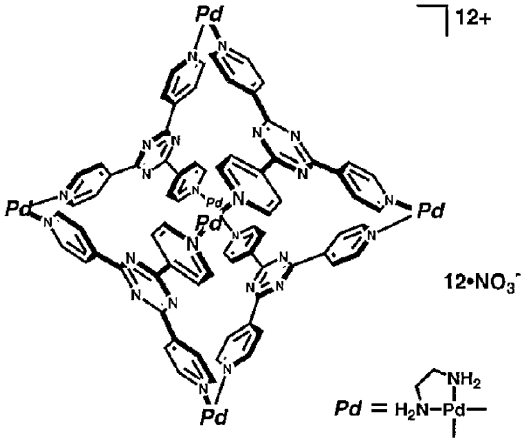
(**98**)



(**99**)



(**100**)



(**101**)[549]

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7. Conclusions

A myriad of the tri- and high-nuclearity palladium(II) and platinum(II) complexes have been reported during the last 15 years or so. The metal square planes in these complexes are arranged in several different ways, yet one can find many other ways to assemble them in high-nuclearity complexes. An understanding of the factors contributing to the nuclearity of the complexes (*e.g.*, $[Pd(SR)_2]_n$ (n = 6 or 8); $[Pd(\mu\text{-SeR})(\eta^3\text{-allyl})]_n$ (n = 2 or 3)), would assist in developing a better synthetic strategy. Self-assembled molecules and dendrimers can now, however, be designed with a reasonable confidence. Although some of these complexes have been used in catalysis, materials science and for molecular recognition, *etc.*, the chemical reactivity aspects and their application in catalysis, biology, materials science are emerging. It is hoped that the present review will provide an impetus for further growth and development of the chemistry of these complexes.

Acknowledgements

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