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COORDINATION CHEMISTRY REVIEWS

12. Platinum 1993

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CONTENTS

INTRODUCTION

The coordination chemistry of platinum reported during the year 1993 has been reviewed. Although this account does not intend or claim to be comprehensive, examples have been selected to represent important features. Only the primary journals are covered and were searched using both platinum (and related) as a keyword and being present in the title. The review covers the chemistry of platinum in its 0 $\rightarrow$ +4 oxidation states, but does not include the catalytic activity of platinum complexes, complexes containing only Pt-C bonds or complexes containing nucleotide or nucleoside bases. Classification of the complexes is according to the oxidation state and donor atom. For complexes containing mixed donor sets the priority ordering P>N>S applies, and neutral donors have priority over charged donor atoms; mixed donor didentate ligands are treated separately.

12.1 PLATINUM(IV)

Reaction of $[PtMe_2(phen)]$ with RE-ER (ER = OH, OC(O)Ph, SMe, SPh, SePh) gives $[Pt(Me)_2(ER)_2(phen)]$ (**1**) as a mixture of *trans*- (major) and *cis*- (minor) isomers. For (**1**; ER = SePh) the solid state structure was determined by X-ray crystallography [1]. Treatment of the platinum(IV) iodide $[PtMe_3(\mu\text{-}I)]_4$ with the aminothiol $HS(CH_2)_2NEt_2$ in methanol afforded the trinuclear species $[(PtMe_3)_3\{(\mu\text{-}I), \mu\text{-}S(CH_2)_2NHEt_2\}_2]$ I (**2**). The complex displays a cubane type structure but with one less $PtMe_3$ vertex, as revealed by an X-ray analysis [2].

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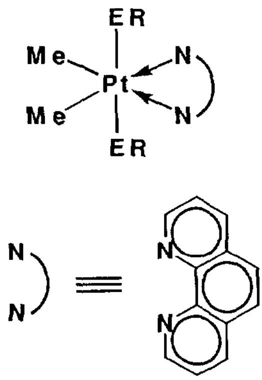
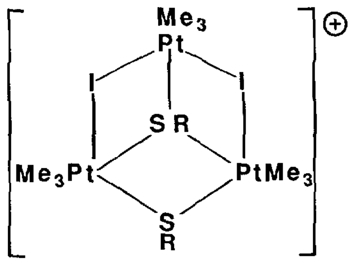
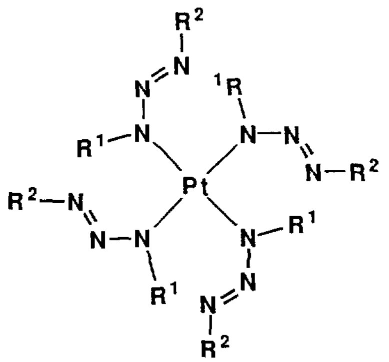


(1)

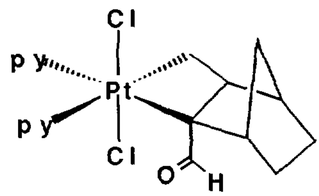


(2; $R=CH_2CH_2NHEt_2$)

A novel *tetrakis*(arylalkyltriazenido) derivative of platinum(IV) has been reported. The complex $[C_6H_5NNN(CH_2)_5CH_3]_4Pt$ (**3**) was characterised by ^{31}Pt NMR spectroscopy and single crystal X-ray crystallography [3]. The first crystal structure of a platinum(IV)-cyclobutane bearing an electron withdrawing aldehyde functionality (**4**) has been described [4].



(3; $R_1= (CH_2)_5CH_3$, $R_2=C_6H_5$)



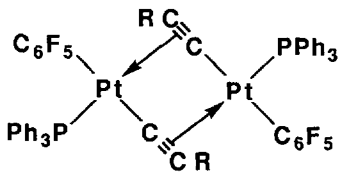
(4)

Electrospray mass spectra have been obtained for a variety of organo-platinum(IV) compounds containing polydentate *N*-donor ligands. In every case the intact ion was observed as the base peak at low ion source energies [5]. The compounds $Cs_2[MCl_6]$ (M = Rh, Pt, Ir) have been shown to be isomorphous by powder diffraction [6].

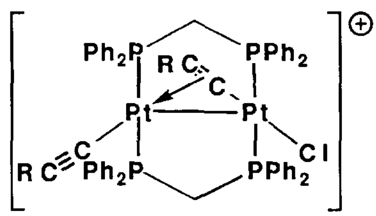
12.2 PLATINUM(II)

12.2.1 Complexes with phosphine donor ligands

The dinuclear, double-bridged acetylide complexes $[Pt(\mu\text{-}C{\equiv}CR)(C_6F_5)(PPh_3)]_2$ (R = Ph, Bu, $SiMe_3$) (**5**) have been synthesised from *trans*-$[Pt(C{\equiv}CR)_2(PPh_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$. Treatment of the dimeric complexes with neutral ligands (L = py, PPh_3) produced the mononuclear species *trans*-$[Pt(C_6F_5)(C{\equiv}CR)(PPh_3)(L)]$. The solid state structure of (**5**; R = Ph) was established by X-ray diffraction methods [7]. The dinuclear platinum(II) complexes $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}CPh)(C{\equiv}CPh)_2]^+$ and $[Pt_2(\mu\text{-dppm})_2(\mu\text{-}C{\equiv}C^tBu)(C{\equiv}C^tBu)Cl]^+$ (**6**) containing bridging and terminal acetylide ligands have been prepared by reaction of $[Pt(\text{dppm-}P,P')_2]Cl_2$ with $[Hg(PhC{\equiv}C)_2]$ or $[Hg(^tBuC{\equiv}C)_2]$ respectively. The crystal structures of both complexes were reported [8].

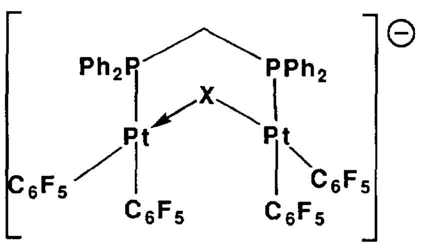


(**5**)

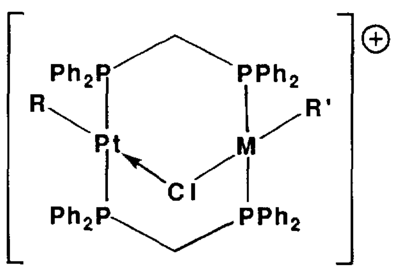


(**6**)

Reaction of $[Pt_2(C_6F_5)_4(\mu\text{-}X)_2]^{2-}$ (X = Cl, Br, I) with dppm at room temperature affords $[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]^{2-}$ as the kinetic products. Subsequent reaction of these di-anions with $AgClO_4$ gave the mono-anions (**7**). The bridging system in these complexes is exceptionally stable, and was not cleaved by anionic (X^-) or neutral ligands (*e.g.* py, PPh_3) [9]. Symmetrical and unsymmetrical dppm-bridged platinum(II) complexes (**8**) have also been prepared, in this instance by reaction of compounds of the form $[PtR(\text{dppm-}P,P')(\text{dppm-}P)]^+$ with [PtRCl(cod)] and [PtR'Cl(cod)], respectively. In a similar series of reactions, the mixed metal complexes $[PtPdRMe(\mu\text{-}Cl)(\mu\text{-dppm})_2]PF_6$ were obtained upon addition of [PdMeCl(cod)] to $[PtR(\text{dppm-}P,P')(\text{dppm-}P)]^+$ [10].

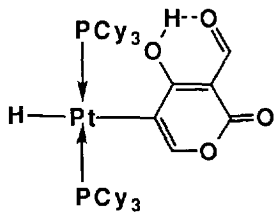


(**7**)



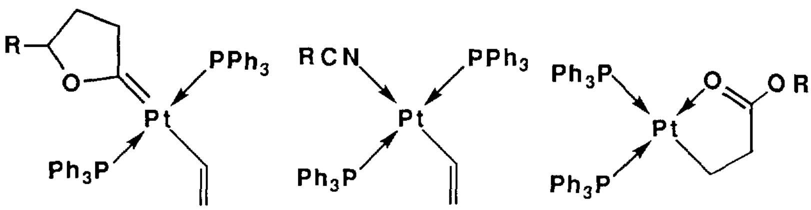
(**8**) M=Pd, Pt; R=Me, Et, Ph
R'=Me, Et, Ph

The formylketenyl platinum complex *trans*-$[PtH\{\eta^1\text{-}C(CHO)CO\}(PCy_3)_2]$ reacts with acids to cleave the Pt-C bond and generate the species $C_3H_2O_2$, which is subsequently trapped by an excess of the starting material. The reaction gave rise to *trans*-$[PtH(C_6H_3O_4)(PCy_3)_2]$ (**9**), where $C_6H_3O_4$ is an α-pyrone ligand σ-bonded to platinum; the solid state structure of (**9**) was established [11].



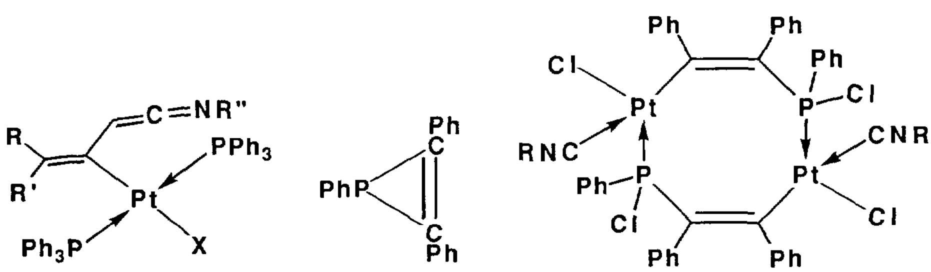
(9)

The reaction of (2-propenyl)*bis*(triphenylphosphine)platinum(II) triflate with unsaturated organic substrates has been investigated. Alkynols {3-butyn-1-ol and (±)-4-pentyn-2-ol} produce the vinylcarbene species (**10**), whilst reaction with nitriles (acrylonitrile and ethyl cyanoacetate) affords the *N*-bound nitrile complexes (**11**). Reaction with methyl- and ethyl acrylates, on the other hand, results in the formation of the chelated compounds (**12**); the structure of (**12**; R = Me) was determined using X-ray diffraction [12].



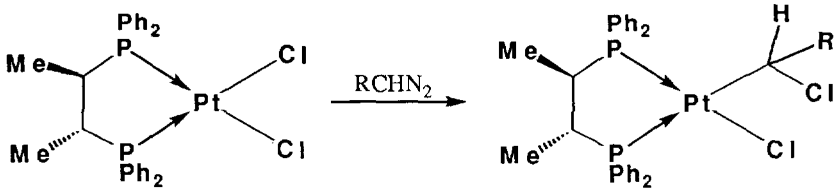
(10^+; R=H, Me) (11^+) (12^+; R=Me, Et)

Insertion reactions of isocyanides into the M-C bond of (σ-allenyl)platinum(II) complexes have been reported. When the R groups of the allenyl ligand are small, new (metallovinyl)ketenimine compounds *trans*-[PtX{C(CRR')(CH=C=NR")}$(PPh_3)_2$] (**13**) are formed, whilst with large R groups the insertion of the isocyanide is sterically hindered and ionic *trans*-[Pt{C(H)=C=CRR'}(CN^{t}Bu)$(PPh_3)_2$]Br results [13]. A new type of ligating behaviour of the phosphirene ring system (**14**) has been described, in which novel dimeric platinum(II) chlorophosphane complexes (**15**) result from Pt-Cl bond insertion and phosphirene ring opening [14].



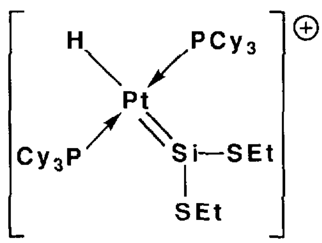
(13) (14) (15)

Dichloroplatinum(II) complexes containing chelating *bis*-phosphine ligands react with diazo-compounds to give Pt-Cl insertion products. Thus, [$PtCl_2$(*S,S*-skewphos)] reacted with Me_3SiCHN_2 to give [PtCl(*S*-$CHClSiMe_3$)(*S,S*-skewphos)] with high diastereoselectivity [15]. In a similar series of reactions, [$PtCl_2$(*R,R*-skewphos)] reacted with $RCHN_2$ {R = $SiMe_3$, $P(O)(OMe)_2$, CO_2Me} to give mono-insertion products (**16**) in which (*R*) stereochemistry is preferred for the newly created chiral centre [16].



(**16**)

Acetylenes, RC≡CR (R = Ph, Pr), insert into the Pt-Si bond of *trans*-[PtX($SiMe_3$)(PEt_3)$_2$] (X = Br, I) to give *trans*-[PtX{C(R)=C(R)$SiMe_3$}(PEt_3)$_2$]; the structure of *trans*-[PtX{C(Ph)=C(Ph)$SiMe_3$}(PEt_3)$_2$] was determined by X-ray crystallography [17]. A Fischer-type silyene complex of platinum, *trans*-[Pt(H){=Si(SEt)$_2$}(PCy_3)$_2$]BPh_4 (**17**), has been prepared from *cis*-[Pt(H){Si(SEt)$_3$(PCy_3)$_2$] upon reaction with Me_3SiOTf and $NaBPh_4$. The solid state structure of the silyene complex was reported [18].

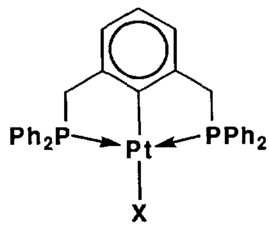


(**17**)

The syntheses of two series of cyclopentadienyl complexes have appeared. In the first account, reaction of [Pt(OTf)$_2$(P-P)] (P-P = dppm, dppe, dppp) with Tl(C_5H_5) to produce the ionic compounds [Pt(η^5-C_5H_5)(P-P)]OTf was described [19]. In the second report, the neutral compounds [Pt(η^5-C_5H_4R)(Ph)(L)] (Y = H, Me; L = PCy_3, PPh_3) were obtained directly on treatment of [Pt(Ph)(μ-OH)(L)]$_2$ with cyclopentadiene or methylcyclopentadiene [20]. A range of complexes of the type *cis*-[Pt(Ar)$_2$(PPh_3)$_2$] (Ar = aryl group) with substituents of different van der Waals volumina and electronic character in both *ortho*-positions of each platinum bonded phenyl ring have been synthesised, and studied with respect to substituent influences on their photochemical reactivity [21].

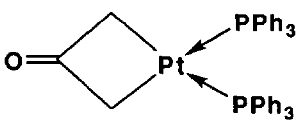
The *trans*-spanning ligand 1,3-C_6H_4(CH_2PPh_2)$_2$ undergoes cyclometallation with either [PtMeCl(cod)] or [$PtCl_2$(cod)] to give (**18**; X = Cl), containing the ligand bound to platinum in a

P,C,P'-tridentate fashion. Successive treatment of (**18**; X = Cl) with $AgBF_4$ and KOH gives (**18**; X = OH) which reacts with CO to produce the hydroxycarbonyl (**18**; X = CO_2H). The solid state structure of the hydroxycarbonyl species was determined using X-ray diffraction methods [22].

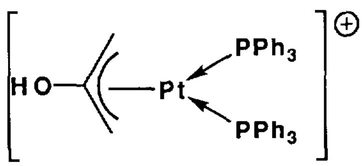


(**18**; X=Cl, OH, CO_2H)

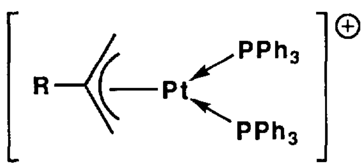
Treatment of π-allyl platinum(II) complexes bearing a methoxymethoxy group at the 2-position with base gives oxodimethylmethane complexes (**19**) in contrast to 2-hydroxy substituted π-allyl complexes *via* acidic hydrolysis (**20**) [23]. A versatile route to 2-substituted π-allyl complexes, *e.g.* (**21**), from addition of hard and soft nucleophiles to the cationic η^3-propargyl complex (**22**) has been described [24].



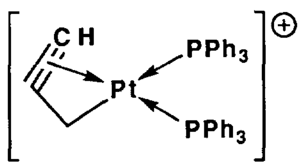
(**19**)



(**20**)

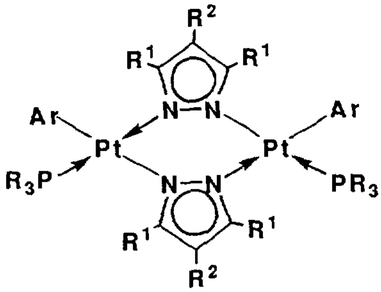


(**21**; R=OMe, SPh, OAc)



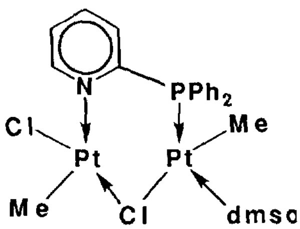
(**22**)

A series of dinuclear pyrazolato-bridged platinum(II) complexes of the form $[Pt_2Cl_2(\mu\text{-}L)_2(PR_3)_2]$ (HL = pz, 3,5-Me_2pz; PR_3 = PEt_3, PMe_2Ph, $PMePh_2$) have been prepared by reaction of the corresponding acetate-bridged analogue with HL. A single crystal structure analysis of a representative complex, $[Pt_2Cl_2(\mu\text{-pz})_2(PMe_2Ph)_2]$, was also reported [25]. In a similar account, the synthesis of a second series of pyrazolato-bridged platinum(II) dimers was described. Thus, treatment of $[Pt_2(Ar)_2(\mu\text{-Cl})_2(PR_3)_2]$ (Ar = Ph, C_6H_4Me-4, C_4H_3S-2; PR_3 = PBu_3, PMe_2Ph, $PMePh_2$) with HL (L = pz, 3,5-Me_2pz, 3,4,5,-Me_3pz) and NaOH gave $[Pt_2(Ar)_2(\mu\text{-L})_2(PR_3)_2]$ (**23**) [26].



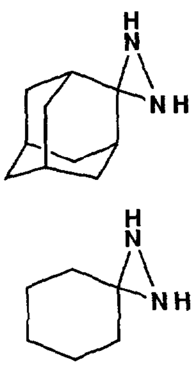
(23) R^1=R^2=H,
R^1=R^2=Me,
R^1=Me, R^2=H

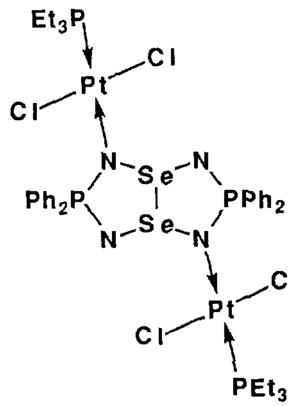
Reaction of *cis*-[$PtCl_2(dmso)_2$] with Ph_2Ppy gave as the main product *cis*-[$PtCl_2(Ph_2Ppy)(dmso)$], in which Ph_2Ppy is η^1-bonded through phosphorus to platinum. However, treatment of *cis*-[$PtCl_2(Ph_2Ppy)(dmso)$] with [$PtMe_2(dmso)_2$] gave the dinuclear platinum(II) compound [MeClPt(μ-Cl)(μ-Ph_2Ppy)PtMe(dmso)] (**24**) and the Pt(I)-Pt(I) dimer [Pt_2Cl_2(μ-$Ph_2Ppy)_2$]; both were structurally characterised by an X-ray diffraction study [27].



(24)

The preparation and characterisation (by X-ray diffraction and multinuclear NMR spectroscopy) of mono- and bis-platinated derivatives of two diaziridines (**25**) has been reported [28]. Reaction of 1,5-$Ph_4P_2N_4Se_2$ with [$PtCl_2(PEt_3)_2$] produced the η^1-N-bonded adducts [$PtCl_2(PEt_3)]_n$(1,5-$Ph_4P_2N_4Se_2$) [n = 1; 2 (**26**)] [29].

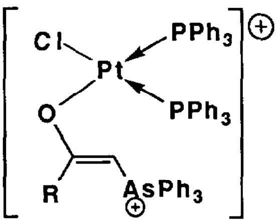




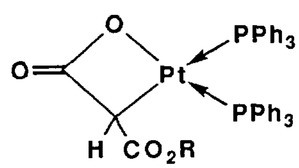
(25) (26)

Treatment of $[PtX_2\{P(CH_2OH)_3\}_2]$ (X = Cl, Br) with AgY (Y = NO_3, BF_4, PF_6, ClO_4) in H_2O gave three species, which were identified as $[Pt(OH_2)_2\{P(CH_2OH)_3\}_2]^{2+}$, $[Pt_2(\mu\text{-}OH)_2\{P(CH_2OH)_3\}_4]^{2+}$ and $[Pt_3(\mu\text{-}OH)_3\{P(CH_2OH)_3\}_6]^{3+}$. The mononuclear product $[Pt(OH_2)_2\{P(CH_2OH)_3\}_2]^{2+}$ reacted further with *N*-donor ligands to afford complexes of the form $[PtL_2\{P(CH_2OH)_3\}_2]^{2+}$ (L_2 = 2py, bpy, phen) [30].

A series of cationic platinum(II) complexes $[PtCl(dppe)\{OC(R)CH(AsPh_3)\}]BF_4$ (R = Me, Ph, OMe) (**27**) in which the carbonyl stabilised arsonium ylides are coordinated to the metal centre have been described [31]. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with dialkyl malonate in the presence of Ag_2O gave new platinalactone complexes (**28**), *via* a cyclisation reaction [32].

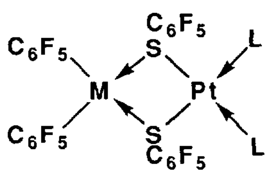


(**27**)



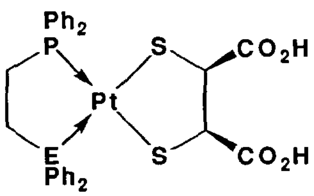
(**28**; R=Me, Et)

The crystal structures of the complexes $[Pt(Et)(\beta\text{-dik})(PPh_3)]$ (β-dik = acac, monothioacetylacetonate) have been determined, and compared to those for $[Pd(Me)(\beta\text{-dik})(PPh_3)_2]$ [33]. In a series of related papers, the preparation and characterisation of *bis*(phosphine)platinum(II) complexes containing group 16 ligands has appeared [34-36]. Thus, for example, $[Pt(EPh)_2(dppe)]$ (E = O, S) have been prepared by reaction of the parent chloro-complex with NaOPh or $PhSH/Bu_2NH$, respectively, while $[Pt(SePh)_2(dppe)]$ was formed by oxidative addition of Ph_2Se_2 to $[Pt(C_2H_4)(dppe)]$ [34]. The ability of complexes of this type to act as didentate 'ligands' towards other metal species was demonstrated [35, 36]. For example, *cis*-$[Pt(SC_6F_5)_2L_2]$ (L_2 = dppm, dppe, $2PPh_3$) when treated with *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd, Pt) yielded the geminal homo- or hetero-dinuclear compounds (**29**) [36].

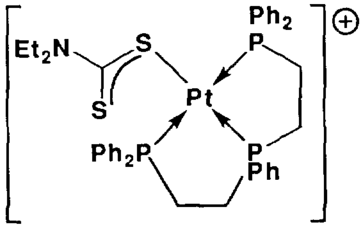


(**29**; M=Pd, Pt)

The complex $[Pt(H_2dmsucc\text{-}S,S')(L\text{-}L)]$ ($H_4dmsucc$ = dimercaptosuccinic acid; L-L = dppe, 1-diphenylarsino-2-diphenylphosphino ethane) (**30**) have been prepared and characterised [37]. The structure of $[Pt(Et_2dtc)(P_2P')]BF_4$ {Et_2dtc = S_2CNEt_2; P_2P' = $PhP(CH_2CH_2PPh_2)_2$} (**31**) has been established using X-ray diffraction techniques. The short non-bonding distance between platinum and sulfur (2.753(3) Å) indicated the possibility of some interaction between the two atoms in the solid state [38].



(30; E=As, P)



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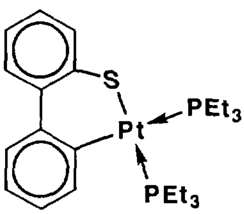
The platinum(0) complex $[Pt(PEt_3)_3]$ inserts (reversibly) into the C-S bond of dibenzothiophene to give the compound (**32**) containing a Pt-S-C linkage. The new complex was characterised by NMR spectroscopy and an X-ray crystal structure determination [39]. The solid state structure of *cis*-$[PtCl_2(SEt_2)\{P(CH_2CH_2CN)_3\}]$ and *trans*-$[PtCl_2\{P(CH_2CH_2CN)_3\}_2]$ have been determined crystallographically. In the latter, the $P(CH_2CH_2CN)_3$ ligands were found to form an 'inverted' umbrella relative to platinum [40]. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with (2,4,6-$^tBu_3C_6H_2$)TeLi•3thf or (2,4,6-$^iPr_3C_6H_2$)TeLi•3thf gave the corresponding, air stable, cis-platinum(II) tellurolates; for example (**33**) whose structure was established using X-ray diffraction [41].



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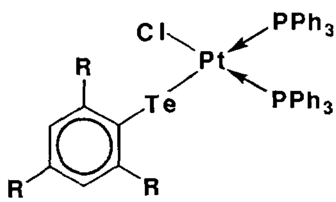
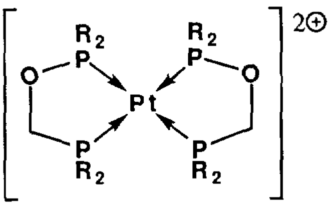


(33; R=^{t}Bu)

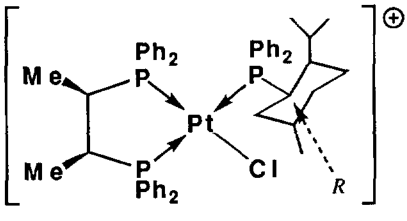


cis-(34; R=CH_2OH)

A convenient one step method for the synthesis of dinuclear platinum(II) phosphine complexes has been reported. The procedure involves direct reaction of $PtCl_2$ and the appropriate phosphine in *p*-chlorotoluene [42]. Addition of 3 equivalents of $P(CH_2OH)_3$ to $Na[PtCl_6]$ or 2 equivalents to $K_2[PtCl_4]$ results in the formation of the platinum(II) complex $[PtCl_2\{P(CH_2OH)_3\}_2]$. Addition of a further equivalent of $P(CH_2OH)_3$ to this complex gives $[PtCl\{P(CH_2OH)_3\}_3]Cl$, while reaction with 2 equivalents gives an unstable species tentatively assigned as $[PtCl\{P(CH_2OH)_3\}_4]Cl$. In the presence of further $P(CH_2OH)_3$, $[PtCl\{P(CH_2OH)_3\}_4]Cl$ gives, amongst other things, the bis(chelate) salts *trans*- and *cis*-$[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ (**34**) [43]. The related phosphine ligand Ph_2PCH_2OH reacted with $[PtCl_2(cod)]$ to give *cis*-$[PtCl_2(Ph_2PCH_2OH)_2]$, the structure of which has been determined by X-ray crystallography [44].

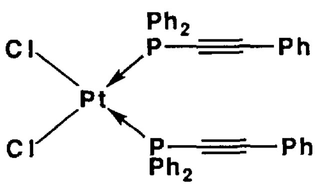
The new *meso*-ligand (R^*,S^*)-2,3-*bis*(diphenylphosphino)butane (achiraphos) has been synthesised and used to prepare the prochiral complex [$PtCl_2$(achiraphos)]. Displacement of one of the enantiotopic chlorine atoms with [1*R*-(1α,2β,5α)]-diphenylmenthylphosphine (*R*-$PMenPh_2$)

and subsequent treatment with NH_4PF_6 gave diastereomeric complexes of the form [PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$ (**35**). The solid state structure of one of the epimers has been determined by X-ray crystallography [45].



(35)

Preparation of the diphenyl(phenylethynyl)phosphine complexes (**36**) has been reported. For (**36**) intramolecular coupling of the phosphinoacetylene ligands occurs on heating to form (**37**), and from (**37**; X = Cl) the free unsymmetrical diphosphine [*o*-$C_{16}H_{10}(PPh_2)_2$], generated by this coupling step, has been isolated [46].



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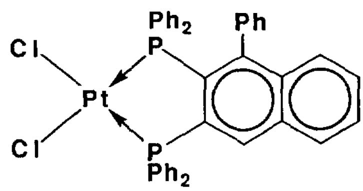
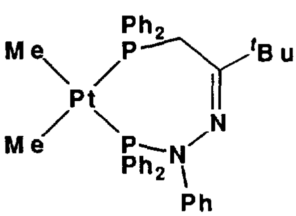


(37)

The series of complexes [PtXX'{η^2-(PPh$_2$)$_3$CH}] (X = X' = Cl, C_6F_5; X = Cl, X' = C_6F_5) have been prepared, and $^{31}P\{^1H\}$ NMR spectra indicate that one of the phosphorus atoms of the triphosphine ligand remains uncoordinated [47]. The new diphosphine PPh$_2$CH$_2$C(^{t}Bu)=N-N(Ph)PPh$_2$ has been synthesised, and treatment with [PtMe$_2$(cod)] affords the expected dimethylplatinum(II) species (**38**) [48].



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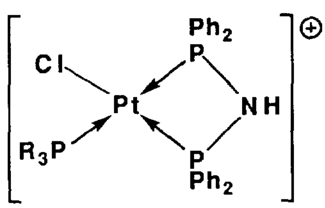
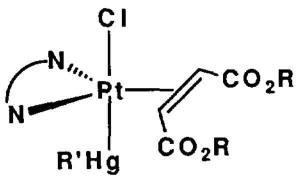


(39)

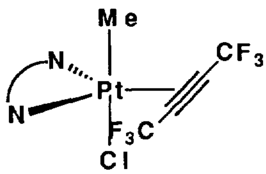
Treatment of *cis*-[PtCl$_2$(PR$_3$)$_2$] {PR$_3$ = PMe$_3$, PMe$_2$Ph, PMePh$_2$, P(^{n}Bu)$_3$, PPh$_3$, PEt$_3$} with dppa {Ph$_2$PN(H)PPh$_2$} afforded the cationic complexes [PtCl(PR$_3$)(dppa)]Cl (**39**), whilst reaction of [$PtCl_2$(dppe)] with dppa gave [Pt(dppa)(dppe)]Cl_2. The molecular structures of [PtCl(PMe_2Ph)(dppa)]Cl, [PtCl{P(^{n}Bu)$_3$}(dppa)]Cl and [Pt(dppa)(dppe)]Cl_2 have been determined by X-ray crystallography and in each instance, reveal dppa acting as a chelate through both phosphorus atoms [49]. The reaction of [$PtCl_2$(cod)] with RN[P(OPh)$_2$]$_2$ (R = Me, Ph) affords similar *P,P'*-chelate complexes [$PtCl_2${RN[P(OPh)$_2$]$_2$}] [50].

12.2.2 Complexes with nitrogen donor ligands

Reaction of organomercury halides HgR'Cl (R' = Me, Et, ^{t}Bu, Ph) with the platinum(0) complexes [Pt(dmphen){(*Z*)-RO_2CCH=$CHCO_2R$}] (dmphen = 2,9-Me_2-1,10-phenanthroline; R = Me, Et, ^{t}Bu) produced 5 coordinate platinum(II) compounds of the form [PtCl(HgR')(dmphen){(*Z*)-RO_2CCH=$CHCO_2R$}] (**40**); the solid state structure of (**40**; R = Me, R' = Me) was established using X-ray diffraction methods [51]. A second series of 5-coordinate platinum(II) complexes of general formula [PtR(Cl)(N-N)(YC≡CY)] (N-N = didentate *N*-donor ligand; Y = CF_3, CO_2Me, CH_2Cl; R = Me, 4-$MeOC_6H_4$), *e.g.* (**41**), have been prepared by treatment of [PtR(Cl)(N-N)] with alkynes. Using a 1:2 alkyne:[PtMe(Cl)(dmphen)] ratio dinuclear species [$Pt_2Me_2(Cl)_2$(YC≡CY)(dmphen)] were isolated, and for the but-2-yne derivative the molecular structure determined crystallographically [52].

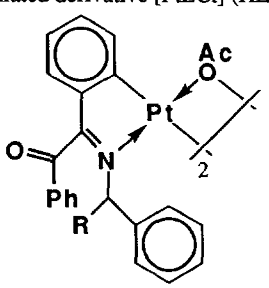


(**40**)

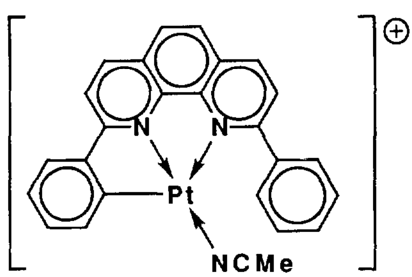


(**41**)

Cyclometallation reactions of *N*-benzyl and *N*-(phenylethyl)-α-benzoylbenzylideneamines with platinum(II) salts have been reported, and the structure of [Pt{C_6H_4(C_6H_5C=O)C=N-$CH_2C_6H_5$}(μ-OAc)]$_2$ (**42**) established [53]. Reaction of [Pt(MeCN)$_4$]$^{2+}$ with dpphen (dpphen = 2,9-diphenyl-1,10-phenanthroline) gave the cyclometallated complex (**43**). The acetonitrile ligand in (**43**) is substitution labile, and can be replaced by nitrogen bases [54]. The synthesis of the cyclometallated derivative [PtLCl] (HL = 6-^{t}Bu-2,2'-bipyridine) has been reported [55].



(**42**)

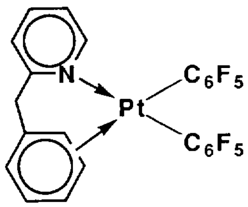


(**43**)

The mixed alkylplatinum(II) complex [Pt(CF_3)(CH_3)(nbd)] reacts with neutral ligands L_2 (L_2 = *e.g.* tmen, 2py, bpy) to afford the corresponding complexes [Pt(CF_3)(CH_3)(L_2)], whilst with MeCN, [Pt(CF_3)(CH_3)(MeCN)$_2$] is formed in equilibrium with starting materials [56]. The kinetics of CN^- substitution at platinum(II) in the series *cis*- and *trans*-[PtCl_2(am)$_2$] (am = *e.g.* Me_2NH, py, 4-CNpy, 4-Clpy, 2-Mepy) has been investigated for the slow step in equation (i) [57].

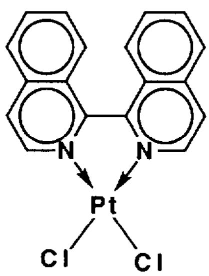
$$[Pt(CN)_2(am)_2] + CN^- \rightarrow [Pt(CN)_3(am)]^- \qquad \text{(i)}$$

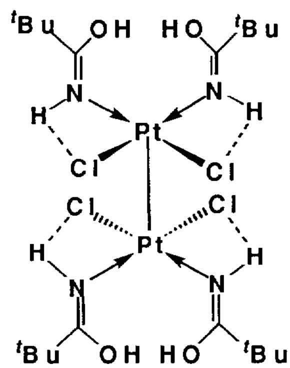
Treatment of *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] with 2-benzyl pyridine gave *cis*-[Pt(C_6F_5)$_2$($PhCH_2py$)] (**44**), which in the solid state, as established by X-ray diffraction, exhibits a weak η^2-benzyl platinum interaction. Subsequent reaction of (**44**) with CO yielded [Pt(C_6F_5)$_2$($PhCH_2py$-*N*)(CO)] which did not contain a Pt-benzyl interaction [58].



(44)

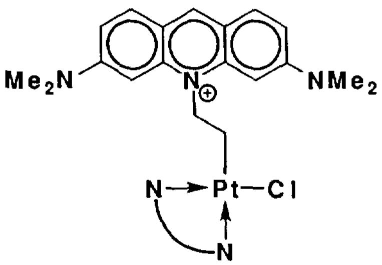
Three platinum(II) complexes of 1,1'-biisoquinoline (biq) have been prepared and their molecular structures determined using X-ray crystallography. In one of these, [PtCl_2(biq)] (**45**) the ligand was found to be didentate, whilst in the complexes [Pt(biq)(L)$_3$] (L = py, 4-NMe_2py) 1,1'-biisoquinoline adopted a unidentate bonding mode [59]. Mono- and bis-nitrile complexes [PtCl_3(NCR)]$^-$ and *cis*- and *trans*-[PtCl_2(NCR)$_2$] (R = ^{t}Bu, Me, Ph) hydrolyse to amidate-amide and mixed amide-nitrile complexes, with the amide ligands in the enol form and *N*-bound to platinum. The complexes are composed of two platinum(II) monomeric units, with a Pt-Pt intermetallic interaction. For example, *cis*-[PtCl_2{HN=C(OH)^{t}Bu}$_2$]$_2$ (**46**) possesses a Pt-Pt distance of 3.165(1) Å [60].



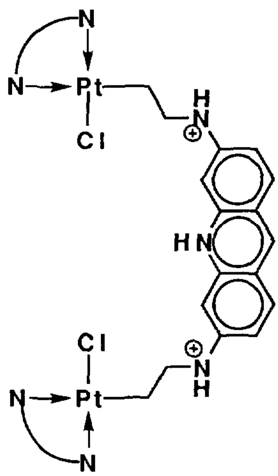


(45) (46)

Reaction of the complex $[PtCl(\eta^2\text{-}C_2H_4)(tmen)]^+$ with acridines {3,6-diaminoacridine and 3,6-*bis*-(dimethylamino)acridine} afforded complexes in which the metal is linked to the polycyclic molecule by an ethylene chain. For 3,6-*bis*-(dimethylamino)acridine attack occurred at the endocyclic nitrogen to give (**47**) whilst for 3,6-diaminoacridine attack occurred at the exocyclic aminic groups to afford (**48**); the structure of the former was established using X-ray diffraction [61].



(47^+)



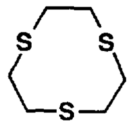
(48^{2+})

Treatment of *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = 4-MePh, 4-CF_3Ph, 2-MePh, Et, *ⁿ*Pr, *ⁱ*Pr, *ᵗ*Bu) with 2 equivalents of $[OCH_2CH_2Cl]^-$ affords the *bis*(Δ^2-1,3-oxazoline) derivatives *cis*- and *trans*-$[PtCl_2\{N{=}C(R)OCH_2CH_2\}_2]$ in high yield [62]. A series of platinum-terpy complexes $[Pt(terpy)L']^{n+}$ {L' = Cl, Br, I, N_3, SCN (n = 1); L' = NH_3 (n = 2)} have been prepared and their spectroscopic and emission properties studied [63]. The ^1H NMR and vibrational spectra for a range of complexes of the general formula $[PtCl_2(am)]$ (am = cycloalkylamine $C_nH_{2n-1}NH_2$; n = 3→8) have been reported [64].

12.2.3 Complexes with sulfur group donor ligands

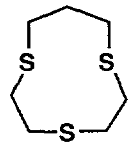
The series of complexes *trans*-$[PtCl_2(C_2H_4)L]$ (L = quinoline *N*-oxide (QNO), isoquinoline-*N*-oxide, 4-ClQNO, 2-MeQNO, 4-MeQNO) have been prepared by addition of L to Zeise's salt. Subsequent reaction of $[PtCl_2(C_2H_4)(4\text{-MeQNO})]$ with L' (L' = CO, PPh_3, py) afforded *trans*-$[PtCl_2(L')(4\text{-MeQNO})]$ [65].

An account detailing the synthesis of a range of complexes containing the potentially tridentate ligand 1,4,7-trithiacyclononane, [9]aneS_3 (**49**), has appeared. The complexes $[PtRR'\{[9]aneS_3\}]$ (R = R' = Me, Et, CH_2CMe_3, CH_2SiMe_3, Ph; R = Me, R' = CH_2SiMe_3; R = Cl, R' = CH_2SiMe_3) were prepared by displacement of cod or nbd from appropriate precursors, and for $[PtPh_2\{[9]aneS_3\}]$ the molecular structure was established by X-ray crystallography [66]. In two related reports, the complexes $[Pt\{(\mathbf{50})\}_2]^{2+}$ [67] and $[Pt\{(\mathbf{51})\}]^{2+}$ [68] were prepared and structurally characterised using X-ray diffraction methods.



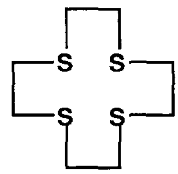
[9]aneS_3

(49)



[10]aneS_3

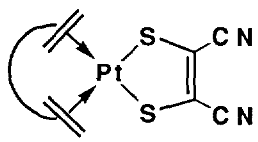
(50)



[12]aneS_4

(51)

The synthesis, characterisation, X-ray structure determination and emission spectroscopy of **(52)** and **(53)** has been reported. Both complexes were obtained upon reaction of $[PtCl_2(cod)]$ and the corresponding dianionic dithiolate salt [69]. The platinum(II) complexes $[Pt(S_2C)]_2$, $[Pt(S_2C)(py)]$ and $[Pt(S_2C)(PMe_3)]$ **(54)** (S_2C = 1,3-imidazolidinyl-*N,N'*-*bis*(2-benzenethiolate) have been prepared and fully characterised [70].



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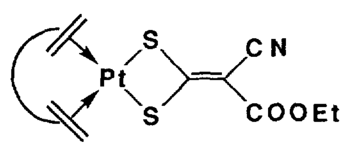

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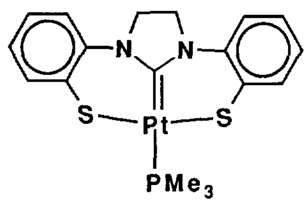
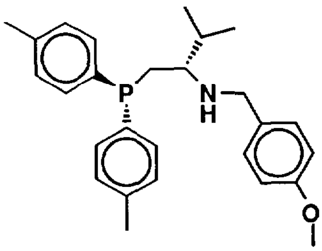


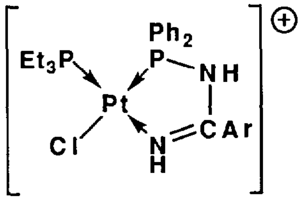
(54)

12.2.4 Complexes with mixed donor ligands

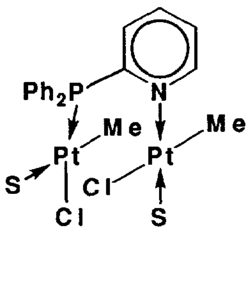
The new *P,N*-didentate ligand **(55)**, derived from valine, has been synthesised and used to prepare the complexes $[PtX_2(\mathbf{55})]$ (X = Cl, I) [71]. Reaction of *trans*-$[PtCl_2\{PPh_2NC(4\text{-}Ar)N(SiMe_3)_2\}(PEt_3)]$ (Ar = 4-MeC_6H_4) with PhSeCl was reported to give **(56)**, containing the *N,P*-chelating ligand $PPh_2N(H)C(Ar){=}N(H)$. The structure of **(56)** was established using NMR spectroscopy and X-ray crystallography [72]. The dinuclear platinum compounds **(57)** and **(58)** have been isolated from the reaction of *cis*-$[PtCl_2(dmso)(PPh_2py)]$ with an equimolar quantity of *cis*-$[PtMe_2(dmso)_2]$; both complexes were the subject of an X-ray diffraction study [27].



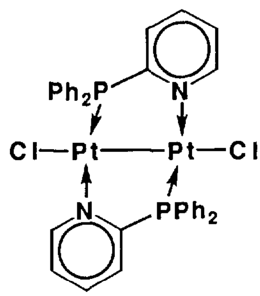
(55)



(56; Ar=4-MeC_6H_4)



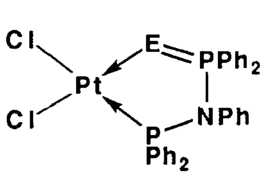
(57; S=dmso)



(58)

The ligands $Ph_2PN(Ph)PPh_2(=E)$ (E = S, Se) (P-E) have been used to prepare the mixed donor complexes $[PtCl_2(P\text{-}E)]$ (**59**), and for E = S the solid state structure has been established [73]. The neutral, dimeric complexes $[\{Pt(C_6F_5)(\mu\text{-}SPPh_2)(PR_3)\}_2]$ (PR_3 = PPh_3, PPh_2Et) and cationic complexe $[Pt(SPPh_2)(PPh_3)_2]ClO_4$ have been reported. For the former the $[SPPh_2]^-$ ligand is present as a *P,S*-bridge whilst in the latter it adopts a *P,S*-chelating bonding mode [74].

Treatment of the chloro-bridged complexes $[Pt_2Cl_4(PEt_3)_2]$ and $[Pt_2Cl_2(MeOcod)_2]$ with the anion $[C(PPh_2)\{P(S)Ph_2\}_2]^-$ affords the complexes $[PtCl(PEt_3)\{C(PPh_2)(P(S)Ph_2)_2\text{-}P,S\}]$ (**60**) and $[Pt(MeOcod)\{C(PPh_2)(P(S)Ph_2)_2\text{-}P,S\}]$, respectively, as a mixture of *cis*- and *trans*-isomers [75]. The synthesis of $[PtCl_2(E\text{-}S)]$ {E-S = (±)$Ph_2ECH_2CH_2S(O)Me$ (E = P, As)} complexes has been reported. In both cases, the ligand acts as an *E,S*-didentate ligand, and M-O bonds are not involved [76].



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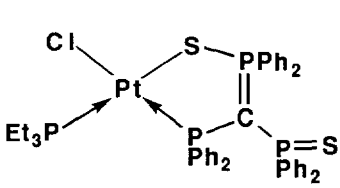
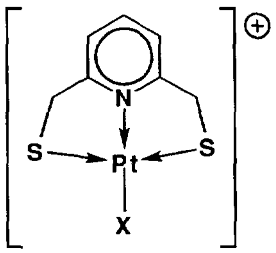
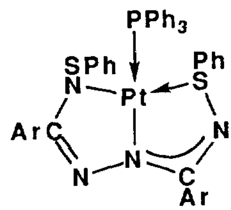


(60)

Reaction of $[Pt(C_6F_5)_2(\mu\text{-}Cl)]_2^{2-}$ with $[C_5H_4NS]^-$ (pyridine-2-thiolate) affords the monomeric complex $[Pt(C_6F_5)_2(C_5H_4NS)]^-$, possessing a $[N\text{-}S]^-$ chelate. Upon reaction of this mono-anionic complex with PPh_3 the species $[Pt(C_6F_5)_2(C_5H_4NS)(PPh_3)]^-$, possessing the ligand in a monodentate *S*-binding mode is obtained [77]. The crystal structures of four platinum(II) complex cations (**61**) containing the organic ligand 2,6-*bis*(methylthiomethyl)pyridine have been determined by X-ray diffraction [78]. Reaction of *trans*-[PhSNC(MeC$_6$H$_4$)N=NC(MeC$_6$H$_4$)-NSPh] with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] gave the platinum(II) complex (**62**) in which the ligand is bonded in a *N,N',S*-tridentate fashion [79]

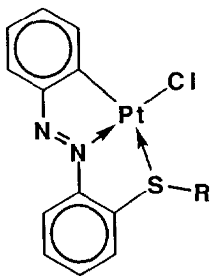


(**61**; X=Cl, Br, SCN)

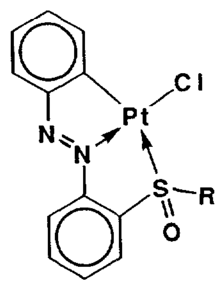


(**62**; Ar=4-MeC$_6$H$_4$)

The thioether and sulphinyl azo-benzene complexes (**63**) and (**64**), respectively, slowly insert oxygen into the Pt-O bond when treated with *m*-chloroperbenzoic acid to produce species containing the *O,N,S*-donor set [80].

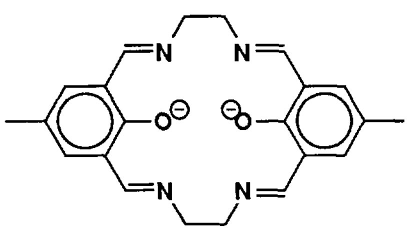


(**63**)



(**64**)

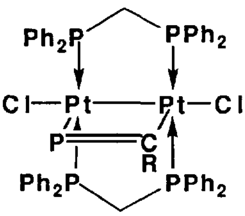
Treatment of platinum salts with L^{2-} (**65**) affords the complex [Pt$_2$(L)]$^{2+}$. For the analogous palladium(II) salt, [Pd$_2$(L)}$^{2+}$, the solid state structure showed the dinucleating macrocycle to be planar with inter-molecular π-ring stacking [81].



(**65**)

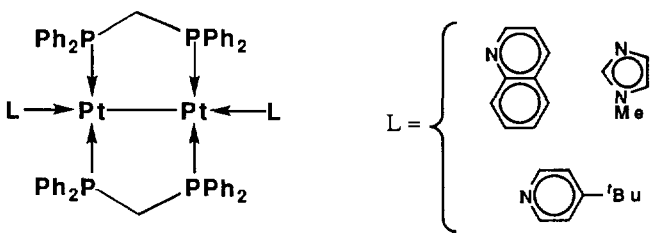
12.3 PLATINUM(I)

The first example of a μ-parallel ligated phospha-alkyne has been reported for the complex [Pt_2Cl_2(μ-dppm)$_2$(μ-^{t}BuCP)] (66). The structure of the molecule was elucidated by ^{31}P and ^{195}Pt NMR spectroscopy [82].



(66; R=^{t}Bu)

Reaction of [Pt_2Cl_2(dppm)$_2$] with 2 L (L = quinoline, *N*-methylimidazole, 4-^{t}butylpyridine) afforded the new compounds [Pt_2(dppm)$_2L_2$]$^{2+}$ (67), whilst reaction with L' = 2,4,6-Me_3pyridine gave [Pt_2(dppm)$_2$(L')Cl]$^+$. For (67; L = quinoline, *N*-methylimidazole) and [Pt_2(dppm)$_2$(L')Cl]$^+$ the solid state structure was determined crystallographically, and the Pt-Pt distances found to be 2.615(1), 2.580(1) and 2.627(2) Å, respectively, thus establishing the presence of a Pt-Pt bond [83].

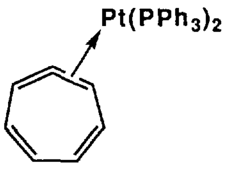


(67^{2+})

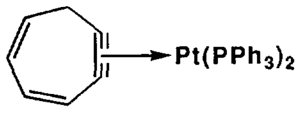
12.4 PLATINUM(0)

Reaction of 1-bromocycloheptene or a mixture of 1-, 2- and 3-bromocycloheptatrienes with ^{t}BuOK in the presence of [Pt(PPh_3)$_3$] led to the predominant formation of Pt(PPh_3)$_2$ π-complexes of the corresponding cyclic allenes, *e.g.* (68). In contrast, reaction of the same halides with LDA in thf in the presence of [Pt(PPh_3)$_3$] gave exclusively Pt(PPh_3)$_2$ complexes of the corresponding cyclic alkynes, *e.g.* (69) [84].

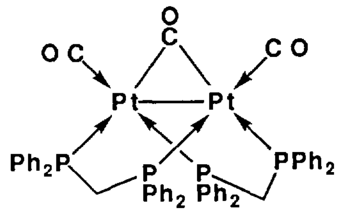
The preparation of [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] and [Pt{*cis*-CH-(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] has been described. The complexes were prepared by reaction of [Pt(η^2-CH_2CH_2)(PPh_3)$_2$] with *trans*- and *cis*-CH(CO_2Et)=CH(CO_2Et), respectively, and for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] the structure was determined from an X-ray analysis [85]. The platinum(0) dimer [Pt_2(μ-CO)(CO)$_2$(μ-dppm)$_2$] (70) has been prepared from [Pt_2Cl_2(μ-dppm)2] *via* $NaBH_4$ reduction under a CO atmosphere and by substitution of a dppm ligand in $[Pt_2(\mu\text{-dppm})_3]$ with CO [86].



(68)



(69)



(70)

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