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COORDINATION
CHEMISTRY
REVIEWS

5. Platinum 1992

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CONTENTS

INTRODUCTION

The coordination chemistry of platinum reported during the year 1992 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 BIDS (Bath Information and Data Service) for both platinum (and related) as a keyword and being present in the title. The review covers the chemistry of platinum in its 0 → +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; neutral, mixed donor didentate ligands are treated separately.

5.1 PLATINUM(IV)

The reaction of iodomethane with the platinum(II) complex $[PtMe_2\{(pz)_2CHMe\text{-}N,N'\}]$ (pz = pyrazol-1-yl) to give the oxidative addition product $[PtMe_3I\{(pz)_2CHMe\text{-}N,N'\}]$ has been

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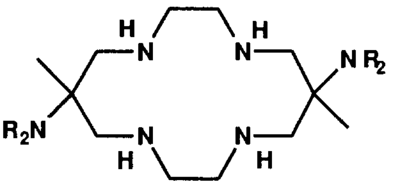
reported. The complex was fully characterised, and ^1H NMR spectroscopic data indicated a solution state structure with the bridgehead methine proton adjacent to the iodine atom. The complex adopts this configuration in the solid state also, as determined from an *X*-ray structural study, with $I \cdots H = 3.1 Å$ [1].

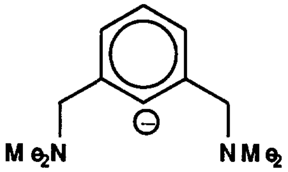
The reduction of platinum(IV) complexes of the form $[PtCl_4(N\text{-}N)]$ (N-N = *N,N'*-chelating diamine ligand) by $[Fe(\eta^5\text{-}C_5H_5)_2]$, I^-, $[Pt(NH_2Et)_4]^{2+}$ or $[Pt(en)(NH_2Et)_2]^{2+}$ has been investigated. The reactions obey second or third order rate laws, and the rate constants increase with increasing steric hindrance at the amine ends of the N-N ligand [2].

Treatment of the platinum(II) complex of the macrocycle 6,13-diammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane (**1** : R = H) with Cl_2 in aqueous solution yielded not only the expected *trans*-dichloroplatinum(IV) complex, but also resulted in complete chlorination of the pendent primary amines. The product formed $[PtCl_2(\mathbf{1}: R = Cl)](ClO_4)_2$ was characterised by a crystal structure analysis, and was found to undergo slow de-chlorination to produce *trans*-$[PtCl_2(\mathbf{1}: R = H)](ClO_4)_2$, also characterised by an *X*-ray structural analysis [3].



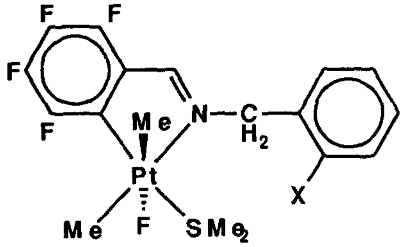
(1)

In an interesting report, *X*-ray photoelectron spectroscopy was employed to determine, and thus compare, the Pt 4f binding energies of the platinum centre in complexes containing the tridentate, monoanionic ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (**2**). As the exact positions of the Pt 4f peaks are a direct indication of the platinum oxidation state, XPS spectra of the complexes $[Pt^{II}I(\mathbf{2})]$, $[Pt^{II}Cl(\mathbf{2})]$, $[Pt^{IV}Cl_3(\mathbf{2})]$ and $[PtI(\mathbf{2})(\eta^1\text{-}I_2)]$ were used to assign a formal oxidation state of +2 for the complex $[PtI(\mathbf{2})(\eta^1\text{-}I_2)]$ [4].



(2)

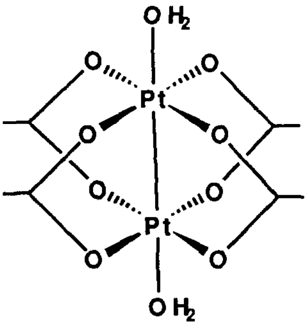
Treatment of the organoplatinum(II) complex $[\{PtMe_2(\mu\text{-}SMe_2)\}_2]$ with imines $(C_6F_5)CH{=}NCH_2(2\text{-}XC_6H_4)$ (X = H, Cl, Br) gave selective activation of the C-F bond to produce the organo-platinum(IV) complex (**3**) [5].



(3)

5.2 PLATINUM(III)

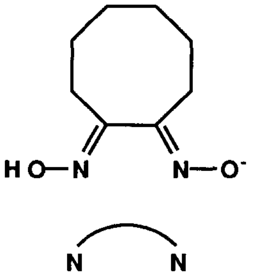
Heating a solution of $K_2[Pt(NO_2)_4]$ in a 2:1 mixture of glacial acetic acid and 1M perchloric acid in air, has been reported to afford the yellow platinum(III) complex $[Pt_2(CH_3CO_2)_4(H_2O)_2](ClO_4)_2$ (4). The solid state structure of this complex was determined by a single crystal X-ray analysis, which revealed an extremely short M-M bond of 2.3905Å [6].



(4)

Controlled chlorination of platinum(II) complexes containing the C_8-carbocyclic α-dioximato ligand $\{C_8H_{12}(=NO)_2H\}^-$ (N-N) (5), or its C_{12} analogue $\{C_{12}H_{20}(=NO)_2H\}^-$, with $PhICl_2$ or p-$ClC_6H_4ICl_2$ gives a 3:1 mixture of $[Pt^{III}(N\text{-}N)_2Cl]_2$ and $[Pt^{IV}(N\text{-}N)_2Cl_2]$. From this mixture, crystalline $[Pt^{III}(N\text{-}N)_2Cl]_2$ (6) was isolated, and its solid state structure determined from a crystallographic study. The complex (6) reacts with further oxidant to produce $[Pt^{IV}(N\text{-}N)_2Cl_2]$, and disproportionates slowly, over several weeks, to $[Pt^{II}(N\text{-}N)_2]$ and $[Pt^{IV}(N\text{-}N)_2Cl_2]$ [7].

The platinum(II) complex dimesitylplatinum(2,2'-bipyridine) is reported to undergo an electrochemically reversible oxidation at *ca.* +0.4V (*vs.* Fc/Fc$^+$) to give a reactive Pt^{III} cation [8]. A single crystal of $[Pt(en)_2](HSq)_2$ (HSq = hydrogen squarate) has been X-irradiated and studied by EPR spectroscopy. The g and ^{195}Pt hyperfine tensors obtained from the angular dependence of the spectrum are consistent with the trapping of a Pt(III) complex, proposed to be $[Pt(en)_2(Sq)](HSq)$ [9].



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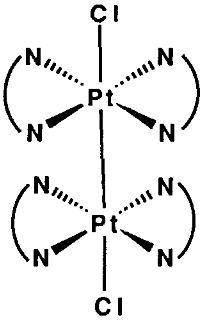

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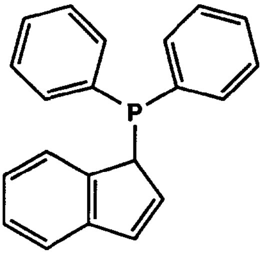
5.3 PLATINUM(II)

5.3.1 Complexes with phosphine donor ligands

Methyl- and halogeno-platinum(II) complexes, containing the diphosphine ligand $(Ph_2PCH_2)_2C{=}CH_2$ (L) have been reported. The dihalogen complexes $[PtX_2(L)]$, upon treatment with MeLi, were converted to the corresponding dimethylplatinum(II) complex $[PtMe_2\{(Ph_2PCH)_2CMe\}]^-$, containing a symmetric, anionic diphosphine. Whilst treatment of $[PtX_2(L)]$ with Cl_2 (X = Cl) or MeI (X = Me) afforded the corresponding platinum(IV) oxidative addition products $[PtCl_4(L)]$ and $[PtMe_3I(L)]$, which were both unstable with respect to reductive elimination. The anionic complex produced above, $[PtMe_2\{(Ph_2PCH)_2CMe\}]^-$, reacts with electrophiles to afford the neutral complexes $[PtMe_2(Ph_2PCHRCMe{=}CHPPh_2)]$ (R = Me, $PhCH_2$, Me_3Si, Ph_2P) [10].

The preparation of (diphenylphosphino)indene (L) (**7**), isolated as two isomers (**7a**) and (**7b**), has been reported. Using both isomeric forms, a series of platinum complexes of the type $[PtCl_xMe_yL_2]$ (x+y = 2) has been isolated and characterised. For the complexes of (**7a**), two pairs of diastereoisomers could be distinguished by NMR spectroscopy [11].



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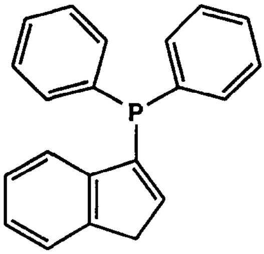
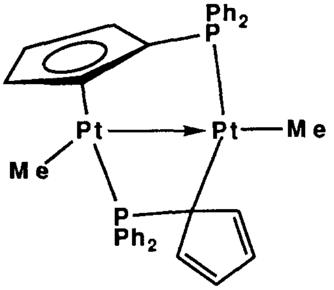
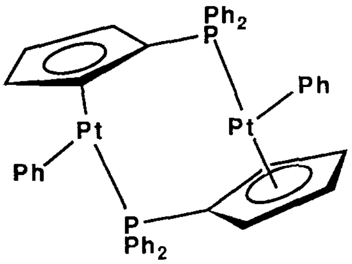


(7b)

The reaction of [PtRCl(cod)] with Tl[$C_5H_4PPh_2$] to yield complexes of the form [Pt_2R_2(μ-$C_5H_4PPh_2$)$_2$] (R = Me, Et, Np, Ph) has been described. For R = Me and R = Np the solid state structures have been determined from single crystal *X*-ray analyses. For the former, a structure exhibiting an η^5- and an η^1-C_5H_4 moiety is observed (**8**), whilst for the latter, both cyclopentadienyl rings are bound in an η^5- fashion (**9**). Further, an equilibrium between the two forms in solution has been proposed [12].



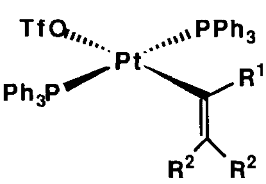
(**8**)



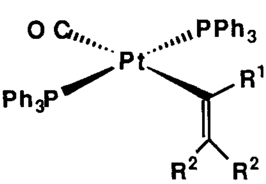
(**9**)

A convenient method for the synthesis of bis(acyl)platinum(II) complexes has been reported. Thus, treatment of *trans*-[Pt(COR)(X)(PPh_2)$_2$] (R = Me, X = Br; R = Et, X = Cl; R = Ph, X = Cl) with ZnR'_2 (R' = Et, Ph) in benzene at 25°C afforded the mono-acyl complexes *trans*-[Pt(COR)(R')(PPh_3)$_2$]. These complexes underwent subsequent carbonylation at 25°C to give the bis-acyl compounds *cis*-[Pt(COEt)$_2$(PPh_3)$_2$] and *cis*-[Pt(COPh)(COEt)(PPh_3)$_2$] [13].

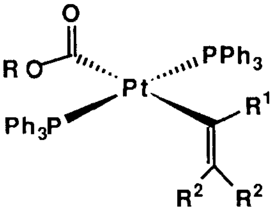
Nucleophilic substitution of the σ-vinyl-Pt(II) triflates (**10**) with CO produced the cationic σ-vinyl Pt(II) carbonyls (**11**), which subsequently reacted with sodium alkoxides to give the neutral σ-alkoxycarbonyl σ-vinyl Pt(II) complexes (**12**). Reaction of (**10**: $R^1 = R^2 = H$) with NaOEt, however, produced the σ-vinyl Pt(II) hydride *trans*-[Pt(H){C(Me)=CH_2}(PPh_3)$_2$] rather than the expected ethoxide. All complexes were fully characterised, including a single crystal *X*-ray structure analysis of (**12**: R = Et, R^1 = Me, R^2 = H) [14].



(**10**) R^1=Me, R^2=H
R^1=H, R^2=Me



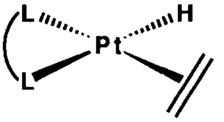
(**11**) R^1=Me, R^2=H
R^1=H, R^2=Me



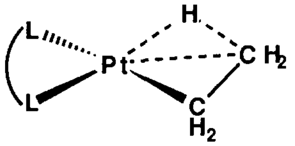
(**12**) R=Et, R^1=Me, R^2=H
R=Me, R^1=H, R^2=Me
R=Me, R^1=Me, R^2=H

The reaction of ethyl diazoacetate with $[PtX_2L_2]$ (X = Cl, Br, I; L_2 = cod, $2PPh_3$, dppm, dppe, dppp, dppb) has been reported to produce the corresponding complexes $[PtX(CHXCO_2Et)L_2]$ as a racemic mixture. When optically active complexes $[PtX_2L^*]$ (X = Cl, I; L^* = for example, *R,R*-DIOP) were treated similarly, analogous complexes were obtained as mixtures of diastereoisomers, but in different proportions. The major diastereoisomer of $[PtCl(CHClCO_2Et)$(*R,R*-DIOP)] was separated by fractional crystallisation and its structure determined from an *X*-ray analysis [15].

The synthesis of electron deficient (fluoroaryl)- and (fluoroalkyl)-phosphine complexes of bis-aryl-platinum(II) has been described [16]. Reaction of $[Pt(\eta^2\text{-}C_2H_4)(L_2)]$ (L_2 = $Cy_2P(CH_2)_nPCy_2$, $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 2,3), $o\text{-}Bu^t_2PCH_2(C_6H_4)CH_2PBu^t_2$ with non-coordinating acids produces a series of cationic complexes which adopt structures exhibiting *cis* ethene/hydride ligands (**13**), or a 2-electron, 3-centre agostic interaction (**14**). The complexes were characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and for (**14**: L_2 = $Bu^t_2P(CH_2)_3PBu^t_2$) the structure was determined by single crystal *X*-ray crystallography [17].

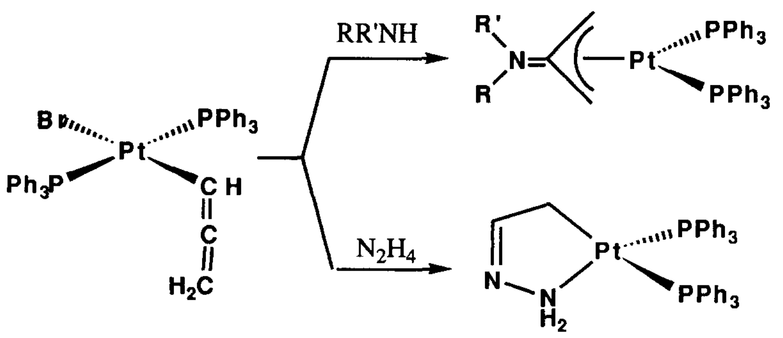


(**13**) L_2=$Cy_2P(CH_2)_nPCy_2$ (n=1,2)
$Bu^t_2P(CH_2)_2PBu^t_2$



(**14**) L_2=$Bu^t_2P(CH_2)_3PBu^t_2$
$o\text{-}(Bu^t_2PCH_2)_2C_6H_4$

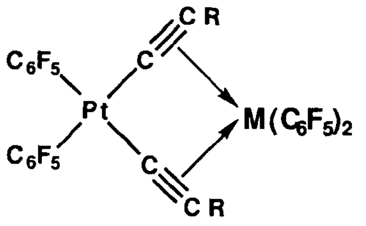
The preparation of (π-allyl)platinum carbonate complexes $[(\eta^3\text{-}2\text{-}MeC_3H_4)\text{-}Pt(PMe_3)_2]^+[OCOOR]^-$ (R = Me, H) has been reported [18]. Treatment of the complex *trans*-$[Pt(CH{=}C{=}CH_2)(Br)(PPh_3)_2]$ with amines or hydrazine results in regioselective addition to the β-carbon of the σ-allenyl group. Thus, reaction with amines produced η^3-azatrimethylenemethane derivatives (**15**), whilst hydrazine gave a platinapyrazoline species (**16**) [19].



(**15**)

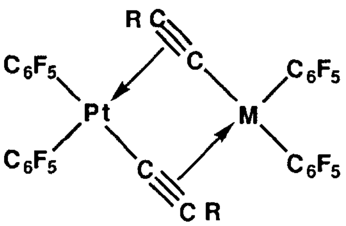
(**16**)

A series of acetylide-bridged, dinuclear Pt-Pt and Pt-Pd complexes has been prepared by reaction of *cis*-$[Pt(C{\equiv}CR)_2L_2]$ (R = Ph, ^{t}Bu; L_2 = $2PPh_3$, dppe, cod) with *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd, Pt). The complexes, of the general form $[\{L_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]$ (**17**), possess $RC{\equiv}C$-Pt-$C{\equiv}CR$ groups acting as a didentate ligand to '$M(C_6F_5)_2$'. Further, the substrate *cis*-$[M(C_6F_5)_2(thf)_2]$ reacted with *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ and $[Pt(C_6F_5)(C{\equiv}CR)_3]^{2-}$ (R = Ph, ^{t}Bu) to give the anionic products $[(C_6F_5)_2Pt(\mu{-}C{\equiv}CR)_2M(C_6F_5)_2]^{2-}$ (**18**) and $[(C_6F_5)(C{\equiv}CR)Pt(\mu{-}C{\equiv}CR)_2Pt(C_6F_5)_2]^{2-}$, respectively. The crystal structures of the complexes $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ and $[(C_6F_5)_2Pt(\mu{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ were also established [20]. Synthesis of the heteronuclear, μ–ethynediyl complexes $[Cl(P_3P)_2MC{\equiv}CM'(PR_3)_2Cl]$ (M = Pt, M' = Pd : R = Me, Et, ^{n}Bu) has been reported [21].



(**17**)

M=Pt or Pd

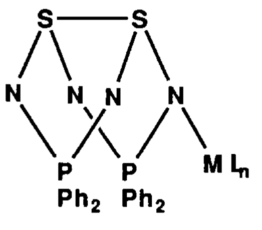


(**18**)

An investigation into the reaction of disilane (H_3SiSiH_3) and 1,2-dimethyldisilane (MeH_2SiSiH_2Me) with *cis*-$[PtH_2(dcpe)]$ has been reported, including the first isolated example of a platinum complex containing terminal di-silanyl (Si_2H_5) groups. Thus, reaction of *cis*-$[PtH_2(dcpe)]$ with H_3SiSiH_3, for example, gave the di-silanyl complex *cis*-$[Pt(Si_2H_5)_2(dcpe)]$, which reacted with further *cis*-$[PtH_2(dcpe)]$ to afford $[Pt(\mu{-}Si_2H_5)(dcpe)]_2$ [22]. In related reports, $[Pt(PEt_3)_3]$ when treated with HMe_2SiSiH_2Me gave *cis*-$[Pt(SiMe_2H)_2(PEt_3)_2]$ [23], and $[Pt(PEt_3)_3]$ with $ArSiH_3$ (Ar = Ph, *p*-tolyl, mesityl) gave *cis*-$[Pt(SiArH_2)_2(PEt_3)_2]$ [24]. The platinum(0) species $[Pt(PEt_3)_3]$ reacted with $ClMe_2GeGeMe_2Cl$ and Me_2GeCl_2, *via* oxidative addition reactions, to give *cis*/*trans*-$[Pt(GeMe_2Cl)_2(PEt_3)_2]$ and *trans*-$[Pt(GeMe_2Cl)Cl(PEt_3)_2]$, respectively; the solid state structure of *cis*-$[Pt(GeMe_2Cl)_2(PEt_3)_2]$ was also reported [25].

Photolysis of $[Pt(C_2O_4)(PEt_3)_2]$ in the presence of amides generates compounds *trans*-$[PtH(HNR)(PEt_3)_2]$ (R = SO_2CF_3, $COCF_3$). Similarly, reaction of the amides with *trans*-$[PtH(Me)(PEt_3)_2]$, *cis*-$[PtMe_2(PEt_3)_2]$ and $[PtMe_2(cod)]$ affords *trans*-$[PtH(HNR)(PEt_3)_2]$, $[PtMe(HNR)(PEt_3)_2]$ and $[PtMe(HNR)(cod)]$ respectively [26].

Treatment of $[PtCl_2(PEt_3)_2]$ with diphosphadithiotetrazocines, 1,5-$R_4P_2N_4S_2$, affords a series of platinum(II) complexes *trans*-$[PtCl_2(PEt_3)(R_4P_2N_4S_2)]$ (R = Me, Et, Ph) in which the $P_2N_4S_2$ ligand is bound *via* nitrogen (**19**). The dithiatetrazocine, 1,5-$(Me_2NC)_2N_4S_2$, and the trithiatetrazocine, $PhCN_4S_3NPPh_3$, also reacted with $[PtCl_2(PEt_3)_2]$ to give the complexes $[PtCl_2(PEt_3)\{(Me_2NC)_2N_4S_2\}]$ (**20**) and $[PtCl_2(PEt_3)(PhCN_4S_3NPPh_3)]$, respectively, which possess the thiatetrazocine ligand bound through nitrogen [27].



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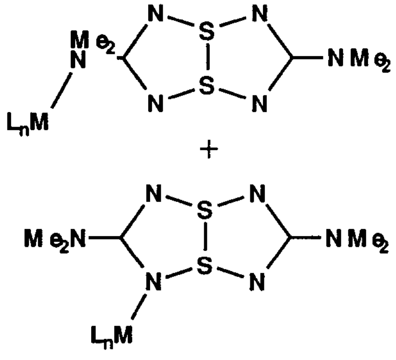
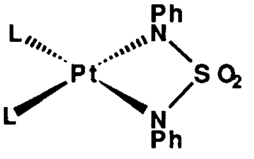


(20)

$ML_n = PtCl(PEt_3)$

The new metallocycles (**21**) and (**22**) have been prepared by reaction of *cis*-$[PtCl_2L_2]$ (L_2 = 2PPh_3, 2$PMePh_2$, 2PEt_2Ph, 2PEt_3, 2$P(NEt_2)Ph_2$, dppm, dppe, dppp, dppb, cod) with *N,N'*-diphenylsulfamide or *N,N',P*-triphenylphosphonic diamide, respectively, and an excess of Ag_2O. The *X*-ray crystal structure of (**21**: L_2 = cod) was reported also [28]. In a related report, the reaction of *N,N'*-diphenylthiourea with *cis*-$[PtCl_2L_2]$ in the presence of Ag_2O afforded complexes (**23**); the presence of a flat Pt-S-C-N ring being established from an *X*-ray structural analysis of (**23**: L_2 = 2PPh_3) [29].



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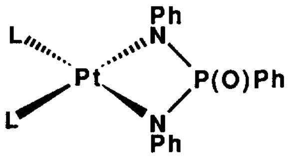

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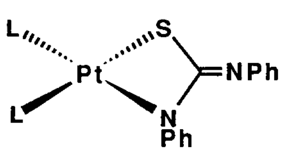

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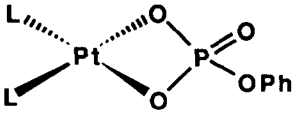
A series of mononuclear, pyridine-2-thiolato (pyS) complexes $[Pt(pyS)_2(PPh_3)_2]$, $[PtCl(pyS)(PPh_3)]$ and $[Pt(pyS)_2(PPh_3)]$, exhibiting a variety of coordination modes, have been synthesised [30]. Dinuclear platinum(II) complexes, of the general formula $[Pt_2Cl_2(\mu\text{-}ER')(\mu\text{-}pz)(PR_3)_2]$ (E = O, S, Se, Te), containing both bridging *N,N'*-pyrazolato and group 16 donors, have been prepared and fully characterised [31]. Mono- and di-nuclear platinum(II) complexes containing the anionic tetrakis(pyrazol-1-yl)borato ligand, $[B(pz)_4]^-$, have been reported [32].

Complexes (**24**), containing a dianionic *O,O*-donor set, have been prepared by reaction of *cis*-$[PtCl_2L_2]$ (L = 2PPh_3, $PMePh_2$, $P(CH_2Ph)Ph_2$, dppe, dppp, dppb) with phenylphosphonic acid $\{P(O)(OH)_2Ph\}$, in the presence of an excess of Ag_2O. The solid state structure of (**24** : L_2 = 2PMe_2Ph) was determined, and interestingly, from an *X*-ray structure determination, a decomposition product of (**24**: L_2 = 2$P(CH_2Ph)Ph$) was found to be the diorthometallated complex (**25**) [33].



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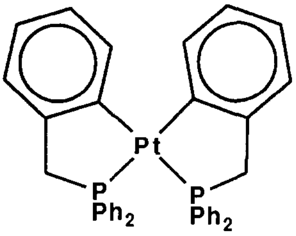
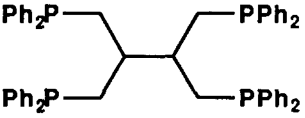


(25)

The triflate complex $[Pt(OTf)_2(dppp)]$ has been prepared by reaction of the corresponding dichloride with methyltriflate [34]. Reaction of $[Pt(SC_5H_9NMe)_2(dppe)]$ with $[PtCl_2(dppe)]$, in organic solvents containing trace quantities of phosgene as an impurity, produced the dinuclear cation $[Pt_2(\mu\text{-}H)(\mu\text{-}S)(dppe)_2]^+$, characterised by an *X*-ray diffraction study [35]. A series of dichloroplatinum(II) complexes containing dithiolato ligands has been reported. The complexes were prepared by treating $[PtCl_2L_2]$ (L_2 = dppm, dppe, dppp, dppb, dcpe) with difunctional thiols (1,2-ethandithiol, 1,3-propanedithiol and 1,2-benzenedithiol) in the presence of base [36].

Mononuclear complexes $[PtCl_2L_2]$ containing chiral bis-phosphine ligands (L_2 = *S*-prolophos, *R*-butaphos; *S*-prolophos = (*S*)-*N*-(diphenylphosphino)-2-{(diphenylphosphinoxy)-methyl}pyrrolidine and *R*-butaphos = (*R*)-1-(diphenylphosphinoxy)-2-{*N*-ethyl-*N*-(diphenyl-phosphino)amino}butane) have been prepared and characterised by ^1H, ^{13}C, ^{31}P, ^{195}Pt and 2-D correlation NMR spectroscopy. In each case, only one conformer is observed in solution, and the solid state structure of $[PtCl_2(S\text{-prolophos})]$ was evaluated [37]. The new tetra-tertiary phosphine ligand (**26**) has been prepared, and reacts with platinum(II) substrates to form the complex $[CH(CH_2PPh_2)_2PtCl_2]_2$ [38]. The symmetrical diphosphene ligand $[2,4,6\text{-}(CF_3)_3C_6H_2]_2P_2$ reacts to form a complex containing the '$PtCl_2(PEt_3)$' fragment, in which the phosphene ligand is η^1-bound [39].



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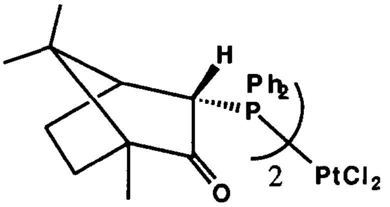
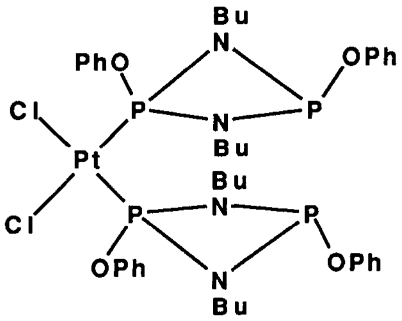
Reaction of *endo*-3-diphenylphosphino-(1*R*)-(+)-camphor (L) with $[PtCl_2(COD)]$ and $[PtCl_2(NCPh)_2]$ gives *cis*-$[PtCl_2L_2]$ and *trans*-$[PtCl_2L_2]$ (**27**), respectively, possessing *endo*-PPh_2 groups. Complexes of the form $[PtCl_2L_2]$ were also formed by heating the bis-camphorphosphine enolate $[Pt(PPh_2C_{10}H_{14}O)_2]$ with HCl [40].

The cyclodiphosphazane *cis*-$[{}^tBuNP(OPh)]_2$ (L) reacts with Pt(II) substrates to afford the mononuclear complex $[PtCl_2L_2]$ (**28**), in which the cyclodiphosphazane is bound to Pt in a monodentate fashion through phosphorus [41]. Metallacrown ether complexes, of the form $[PtCl_2\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}]$ (n = 3-5) have been prepared, and solid state structural determinations have been reported for the complexes with n = 4 and 5 [42]. Several dinuclear

Pt(II) complexes containing 1,1,4,7,10,10-hexaphenyl-1,4,7,10,tetraphosphadecane (P4) (**29**) have been synthesised and characterised by spectroscopy and single crystal *X*-ray crystallography. The complexes are of the form *rac*- or *meso*-$[Pt_2Cl_3P_4]X$, or the thermodynamically more stable form *cis*, *rac*- or *cis*, *meso*-$[Pt_2Cl_4P_4]$ [43].



(**27**)



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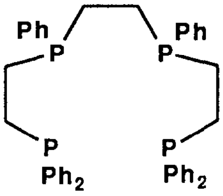
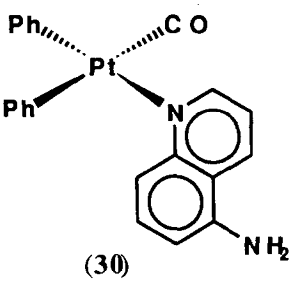


(**29**)

5.3.2 Complexes with nitrogen donor ligands

The new bis-phenylplatinum(II) complexes $[PtPh_2L_2]$ (L_2 = 3,3'-bipyridazine, 4,4'-bipyrimidine, 2,2'-bipyrazine, 1,4,7,10-tetraazaphenanthrene) have been prepared and studied by emission and absorption spectroscopy. The one and two-electron reduced states were generated electrochemically, and the ESR spectrum of the paramagnetic intermediates was measured and found to be consistent with the formulation $Pt^{II}/(L^{-}\cdot)$ [44]. In a separate report, complexes (**30**-**32**) were prepared, and the absorption spectra and luminescence properties described [45].

The preparation of a series of pyrazolyl complexes of general formulation $[PtR_2(HL)_2]$ {R = C_6F_5, HL = Hpz, Hdmpz (3,5-dimethylpyrazole); R = C_6Cl_5, HL = dmpz} and $[NBu_4][Pt(C_6F_5)_2Cl(Hpz)]$ has been reported. Deprotonation of $[Pt(C_6F_5)_2(HL)_2]$ (HL = Hpz, Hdmpz) gives the pyrazole-pyrazolato complexes $[NBu_4][M(C_6F_5)_2(L)(HL)]$ (**33**), exhibiting identical pyrazolyl rings as determined by IR and NMR spectroscopic data and an *X*-ray diffraction study of (**33**: HL = Hpz) [46].



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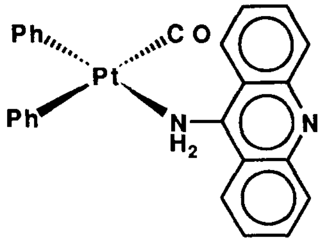

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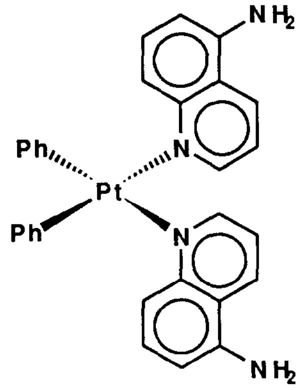

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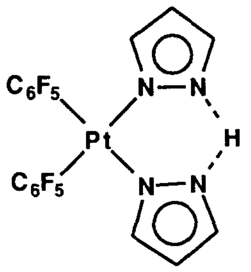

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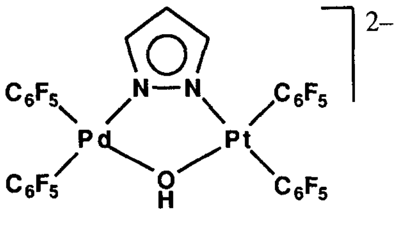
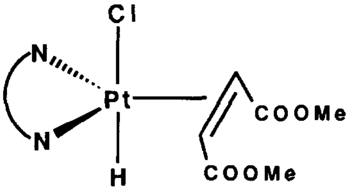
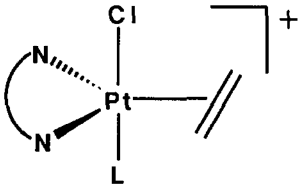


(34)

Treatment of the bridging hydroxy complex $[\{Pt(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with azoles in benzene produces the doubly bridged anions $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L_2)]^{2-}$ (L_2 = pyrazolate, 3,5-dimethylpyrazolate, 3-methylpyrazolate, indazolate), whilst the same reaction in methanol gives the di-μ-azolate anions $[\{Pt(C_6F_5)_2(\mu\text{-}L_2)\}_2]^{2-}$. Complexes of the latter type were alternatively prepared by reaction of $[\{Pt(C_6F_5)_2(\mu\text{-}OMe)\}_2]^{2-}$ with the respective azolates in methanol, and an *X*-ray structural determination of (**34**) established the dinuclear nature of the anion $[\{Pt(C_6F_5)_2\}_2(\mu\text{-}OH)(\mu\text{-}L_2)]^{2-}$ [47].

The preparation, physical properties and photo-physical properties of $[Pt(bph)(Et_2S)]_2$, $[Pt(bph)(MeCN)_2]$, [Pt(bph)(en)] and $[Pt(bph)(py)_2]$ (bph = doubly deprotonated biphenyl) have been described [48]. In a series of papers, a range of neutral (**35**) and cationic (**36**) 5-coordinate platinum(II) complexes were prepared and characterised, in some instances by single crystal *X*-ray diffraction [49-52]. In a separate, but related report, features essential to the formation of 5-coordinate platinum(II) complexes were noted, namely the presence within the coordination sphere of a strong π-accepting ligand [53].

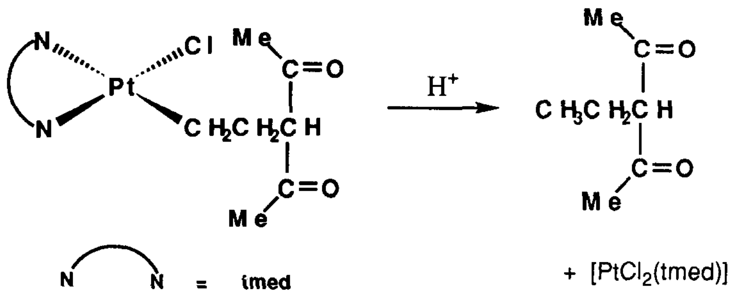




N-N=for example, 2,9-dimethyl-1,10-phenanthroline

(35) (36)

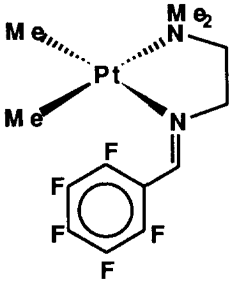
The cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmed)]^+$ reacts with carbon nucleophiles (HL = acetylacetone, ethylacetoacetate, diethylmalonate) in the presence of base to give the corresponding addition products $[Pt(CH_2CH_2L)Cl(tmed)]$ (**37**), possessing a Pt-C σ-bond. Treatment of the complexes with acid (HCl or $HClO_4$) gave the ethylated nucleophile and $[PtCl_2(tmed)]$ [54].



(37)

The activation of aromatic C-X bonds by the organoplatinum(II) complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ has been reported [55, 56]. Thus, for example, the ligand $Me_2NCH_2CH_2N{=}CH(C_6F_5)$ reacts with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to initially form the organoplatinum(II) complex (**38**), which reacts further to produce the platinum(IV) complex (**39**).

In contrast, analogous reactions with the ligands $Me_2NCH_2CH_2N{=}CHAr$ (Ar = 2,3-, 2,4- or 2,6-$C_6H_3F_2$) gave the *N,N'*-bound complexes $[Pt^{II}Me_2(Me_2NCH_2CH_2N{=}CHAr)]$ and subsequently, the compounds $[Pt^{II}Me\text{-}(Me_2NCH_2CH_2N{=}CH)(C_6H_2F_2)]$, in which C-H activation had occurred [55].



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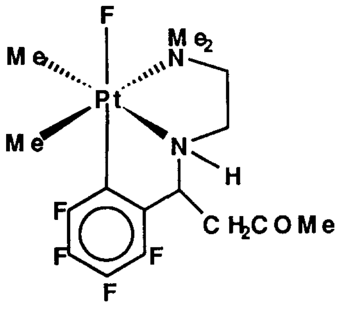
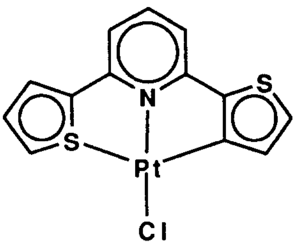


(39)

The potentially tridentate ligand 2,6-bis-(2-thienyl)pyridine (H_2L) reacted with the platinum(II) substrate $K_2[PtCl_4]$ to give cyclometallated complexes exhibiting HL-*C,N* (**40**) and L-*C,N,C'* (**41**) bonding modes [57].



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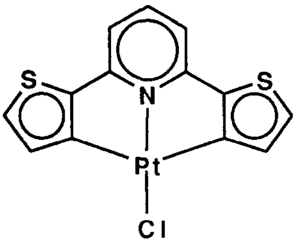
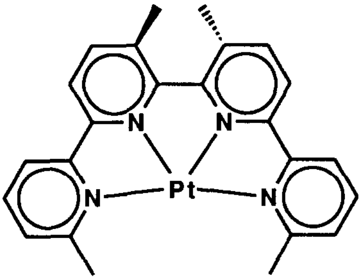


(41)

The kinetics of thioether displacement from *cis*-$[PtPh_2(Et_2S)_2]$ by pyridine or substituted pyridines (py) to yield *cis*-$[PtPh_2(py)_2]$ has been reported [58]. A series of platinum(II) cations containing a *N,N',N'',N'''*-donor set, *eg*. $[Pt(bpy)(py)_2]^{2+}$ or $[Pt(phen)(py)_2]^{2+}$, or a *N,N',N'',C*-donor set, *eg*. $[Pt(Mebpy\text{-}H)(bpy)]^{2+}$, {Mebpy-H = *N*-methyl-2,2'-bipyridinyl-*C*(3),*N'*} have been investigated by cyclic voltammetry, and, in some cases, by epr and UV-VIS-near-IR spectroelectrochemistry [59].

Two cationic platinum(II) quaterpyridine complexes have been synthesised (**42**) and (**43**), and characterised by ^1H NMR spectroscopy and *X*-ray crystallography; both complexes exhibit photoluminescence in the solid state [60]. The Pt(II) complex of the porphyrin based ligand (**44**) has been prepared, and its absorption spectrum and cyclic voltammogram measured [61]. Treatment of the polymeric amine ligand, polyazaridine (PEI) with $K_2[PtCl_4]$ and $[PtCl_2(bpy)]$

gave the single species $[Pt(PEI)_4]^{2+}$ and $[Pt(PEI)_2(bpy)]^{2+}$, respectively, whilst reaction with *cis*-$[PtCl_2(NH_3)_2]$ and $[PtCl_2(en)]$ gave a mixture of products, as determined by UV-VIS and ^{195}Pt NMR spectroscopy [62].



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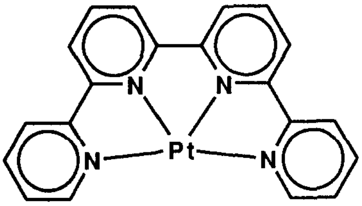

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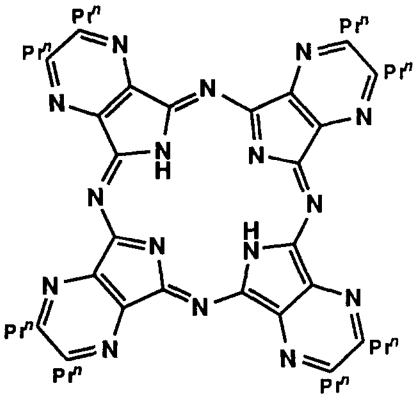

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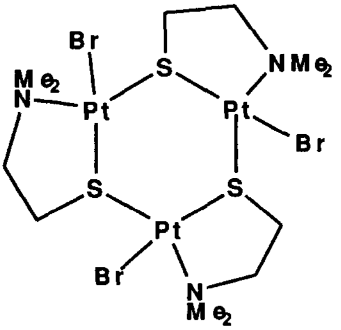

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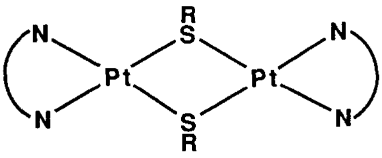
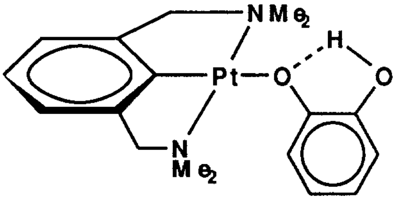


(46)

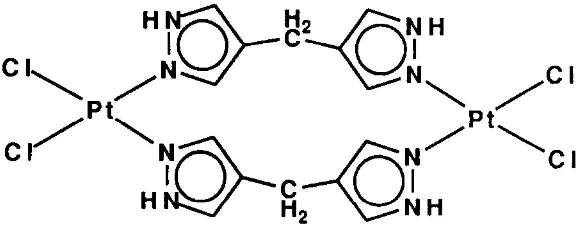
The platinum phenoxide complex [Pt(OPh)(NCN)] (NCN=$C_6H_3\{CH_2NMe_2\}_2$-2,6) has been synthesised by reaction of NaOPh with [Pt(NCN)(H_2O)]BF_4. The complex reacts with excess phenol to form the adduct [Pt(OPh)(NCN)]·HOPh, and the synthesis of the catecholate compound [Pt(NCN)(OC_6H_4OH-2)], possessing an O-H···H hydrogen bond, was reported (**47**) [64]. An account detailing the synthesis and spectral properties of a series of complexes of the general formula [PtCl(R'R''SO)(1,1-diaminomethylcyclohexane)]NO_3 has appeared [65].



(**47**)

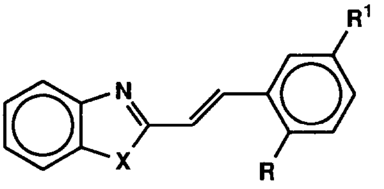
Reaction of 3-ferrocenylpyridine (L) with $[PtCl_4]^{2-}$ gave the square planar complex *cis*-[$PtCl_2(L)_2$], which was structurally characterised by *X*-ray crystallography, and, from cyclic voltammetry, it was shown to undergo two reversible one electron oxidation processes [66]. The compounds [$PtCl_2$(dps)] and [PtCl(MeOdiene)(dps)] (dps = di-2-pyridylsulfide; MeOdiene = Me-OC_8H_{12}, $MeOC_{10}H_{12}$) have been prepared, and IR spectral data suggest that for the latter dps^- ligand is bound in a monodentate fashion. The synthesis of the complexes [Pt(MeOdiene)(dps)]X (X = BF_4, PF_6, ClO_4) was also accomplished, but in this instance the dps ligand in the cation adopted a *N,N'*-chelating bonding mode to platinum [67]. The synthesis and characterisation of three series of dichloroplatinum(II) compounds containing bipyridines disubstituted with perfluoroalkylated side chains has been described [68].

The bis-pyrazolyl ligand 4,4'-dipyrazolylmethane (dpzm) has been employed to prepare dinuclear Pt(II)-Pt(II), Pt(IV)-Pt(IV) and Pt(IV)-Pt(II) complexes containing two bridging dpzm units. The mononuclear complexes *cis*-[$PtCl_2$(dmf)(dpzmH)]Cl and *cis*-[$PtCl_4$(dmf)(dpzm)]Cl·0.5dmf were also prepared, and the solid state structure of γ-[$Cl_2Pt(\mu$–dpzm$)_2PtCl_2$]·2dmf (**48**) was determined from an *X*-ray diffraction study [69].

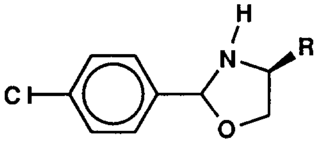


(**48**)

Styrylbenzazole ligands (L) (**49**) based on imidazole, thiazole and oxazole fragments have been used to prepare a series of complexes of general formula *cis*-$[PtCl_2(L)_2]$, in which the benzazole ligands are coordinated to platinum through nitrogen [70]. Oxazolidine based ligands (**50**) have been used to synthesise the optically active compounds *trans*-$[PtCl_2(C_2H_4)$(**50**)$]$; for the complex with R = Et the solid state structure was determined by *X*-ray diffraction [71].



(**49**) X=O, S, NH, N-Me
R, R^1=H, alkyl , aryl



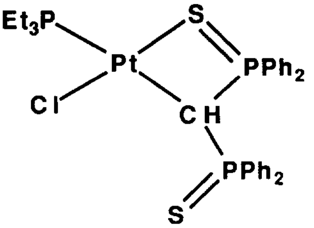
(**50**) R=Me, Et, Bu^i, CH_2Ph, Ph

Treatment of $K_2[PtCl_4]$ or $PtCl_2$ with an excess of RCN affords the nitrile complexes $[PtCl_2(NCR)_2]$ (R = Ph, 4-MePh, 4-(CF_3)Ph, 2-MePh, Me, Et, Pr, Pr^i, Bu^t) as a mixture of *cis* and *trans* isomers, in different ratios depending upon the experimental conditions [72]. A convenient method for the small scale preparation of *trans*-$[PtCl_2(NH_3)_2]$, suitable for the synthesis of ^{15}N-labelled compounds, has been described. Using this method, ^{15}N and ^{195}Pt spectra have been used to characterise *trans*-diammine-platinum(II) compounds with aqua, chloro, nitrato, sulfato, acetato and phosphato ligands [73].

5.3.3 Complexes with sulfur group donor ligands

Treatment of $[NBu_4][\{Pt(C_6X_5)_2(\mu\text{-}Cl)\}_2]$ with $[NBu_4]OH$ leads to the formation of the dinuclear species $[NBu_4][\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (X = F, Cl), which react with weak protic acids (L-LH), *eg*. acetylacetone, to give mononuclear complexes of the form $[NBu_4][Pt(C_6X_5)_2(L\text{-}L)]$ [74]. Reaction of the bis-(phosphine chalcogenides) $CH_2\{P(X)R_2\}\{P(Y)R'_2\}$ (X, Y = O, S, Se) and their corresponding anions $[CH\{P(X)R_2\}\{P(Y)R'_2\}]^-$ with $[PtCl_4\}]^{2-}$, $[Pt_2Cl_4(PEt_3)_2]$ or $[Pt_2Cl_2(PEt_3)_4]^{2+}$ yields a wide variety of coordination compounds. For example, with R = R$'$ = Ph and X = Y = S the following, amongst others, are available: $[PtCl(PEt_3)\{CH(P(S)Ph_2)_2\text{-}C,S\}]$ (**51**) and $[PtCl(PEt_3)\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]^+$ (**52**). In general, the ligands exhibited five different coordination modes, and each has been investigated using NMR spectroscopy [75].

The reaction of thiols (RSH), thioethers (RSR) and disulfides (RSSR) with the platinum compounds [Pt(diene)Cl]Cl (diene = 1,5-diamino-3-azapentane) and [Pt(terpy)Cl]Cl has been investigated by ^1H, ^{13}C and ^{195}Pt NMR spectroscopy [76]. The μ-hydroxo complexes $[\{Pt(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (X = F, Cl) react with amines, in the presence of CS_2, to give the corresponding dithiocarbamate complexes (**53**) [77].



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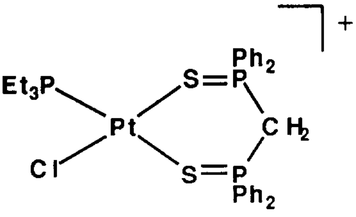

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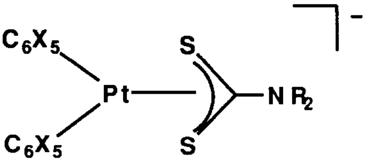
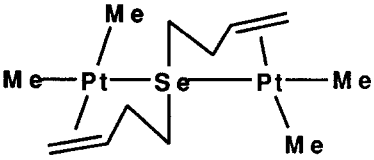


(53) X=Cl or F

The preparation and properties of platinum(II) complexes possessing bulky sulfoxide ligands have been described. Reactions with (MePhSO) gave the expected complex *cis*-$[PtCl_2(MePhSO)]$, whereas sterically more demanding sulfoxides gave mono-sulfoxide products, *eg*. $K[PtCl_3(Ph_2SO)]$; the molecular structures of both these compounds were determined by *X*-ray diffraction [78]. Complex formation between $[Pt(H_2O)_4]^{2+}$ and Me_2S, Et_2S, 1,4-dithiane and 1,4-thioxane has been studied by use of stopped-flow and conventional spectrophotometry [79].

Treatment of $[PtMe_2(SMe_2)_2]$ with 0.5 mole equivalents of the dialkenyl chalcogenoether ligands $E(CH_2CH_2CH{=}CH_2)_2$ (E = S or Se) gave the dinuclear complexes $[Pt_2Me_4\{\mu\text{-}E(CH_2CH_2CH{=}CH_2)_2\}]$ **(54)**, which were characterised by *X*-ray crystallography, and shown to be isostructural. By use of a 1:1 mole ratio of $[PtMe_2(SMe_2)_2]$ and $Se(CH_2CH_2CH{=}CH_2)_2$, the monomeric complex $[PtMe_2\{Se(CH_2CH_2CH{=}CH_2)_2\}]$ was obtained. In this instance, coordination to platinum through Se and one alkene unit was found [80].

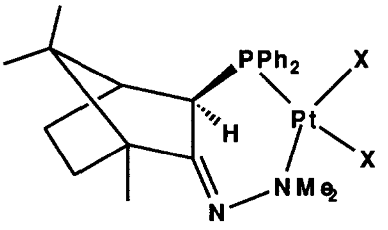


(54)

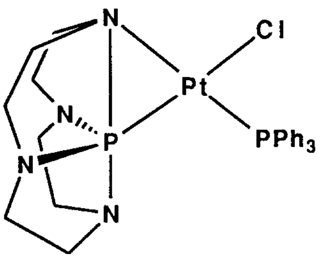
The series of complexes $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeAr)(PR_3)_2]$ (Ar = Ph, 4-MePh, 4-MeOPh, 4-EtOPh; $PR_3 = PBu^n{}_3$, PMe_2Ph) were prepared by treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaTeAr. Subsequent treatment of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeAr)(PR_3)_2]$ with KBr or KI gave the corresponding bromo- and iodo-bridged analogues, and reaction with pyrazole or 3,5-dimethylpyrazole, in the presence of NaOH, yielded $[Pt_2Cl_2(\mu\text{-}pz)(\mu\text{-}TeAr)(PR_3)_2]$; the *X*-ray crystal structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu^n{}_3)_2]$ was determined [81]. The synthesis and spectroscopic characterisation of $[PtX_2(L)_2]$ (X = Cl, Br, I ; L = C_4H_8Te) has been reported [82].

5.3.4 Complexes with mixed donor ligands

Treatment of the *Z*-*exo*-phosphine $PPh_2C_{10}H_{15}NNMe_2$ with $[PtX_2(COD)]$ (X = Cl, Me) gave the compounds (**55**). The *exo*-phosphine converted to an *exo*/*endo*-mixture, and reaction of this mixture with $[PtX_2(cod)]$ gave the corresponding mixed *Z*-*exo*/*endo*-chelate complexes. All the complexes were fully characterised, with particular attention to determining the stereochemistry at C(3) on the camphor residue [83]. The P-N donor ligand complex $[PtCl(\eta^2\text{-}cyclenP)(PPh_3)]$ (**56**) reacted with dppe to form the bis-didentate derivative $[Pt(\eta^2\text{-}cyclenP)(\eta^2\text{-}dppe)]Cl$. On the other hand, reaction with dppm affords the η^1-dppm product $[PtCl(\eta^2\text{-}cyclenP)(\eta^1\text{-}dppm)]$, which, upon treatment with $NaBPh_4$, gives a mixture of compounds, one of which is proposed to be the bis-chelate complex $[Pt(\eta^2\text{-}cyclenP)(\eta^2\text{-}dppm)]BPh_4$ [84].



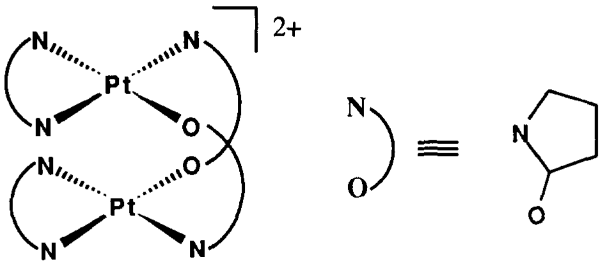
(**55**) X=Cl, Br, Me



(**56**)

Reaction of $[PtCl_2(bpy)]$ with α-pyrrolidine gave the α-pyrrolidonato bridged dinuclear complex $[Pt_2(bpy)_2(\alpha\text{-}pyrrolidonato)_2]^{2+}$. The solid state structure of the complex was evaluated using *X*-ray diffraction techniques, and was shown to adopt a 'head to tail' arrangement of the N-O ligands (**57**) [85].

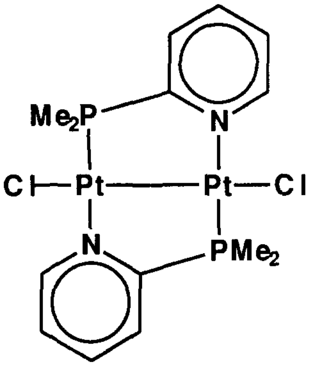
The mono- and bis-chelate ligands bis-[*o*-(methylthio)phenyl]phenylphosphine and tris-[*o*-(methylthio)phenyl]phosphine react with platinum(II) substrates to form $[Pt\{PPh(C_6H_4SMe\text{-}o)_2\}Cl_2]$ and $[Pt\{P(C_6H_4SMe\text{-}o)_3\}_2]^{2+}$ complexes, repsectively, in which the ligands are P/S chelated to platinum [86]. Platinum(II) complexes $[Pt(N,Te)(ClO_4)_2]$, $[Pt(N,Te)](ClO_4)_2$ and $[PtCl_2(N,Te)_2]$ exhibiting *N,Te*-chelation have been described for the mixed donor ligand $1\text{-}(NMe_2)\text{-}2\text{-}(TeC_6H_4OEt)\text{-}4\text{-}MeC_6H_3$ [87].



(57)

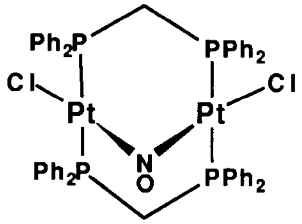
5.4 PLATINUM(I)

The reaction of $[MX_2(R_2Ppy\text{-}P)_2]$ (R = Me, Ph) with $[M'_2(dba)_3]$ (dba = dibenzylideneacetone) has been employed to prepare platinum(I)-platinum(I) and platinum(I)-palladium(I) dimers, $[MM'X_2(\mu\text{-}R_2Ppy)_2]$ [M,M' = Pd(I), Pt(I)]. Initially 'head to head' dimers were formed, but these isomerised to the 'head to tail' form, *eg*. (**58**) [88, 89]. Single crystal *X*-ray diffraction structures were reported for the complexes $[PdPtCl_2(\mu\text{-}Me_2Ppy)_2]$ and $[Pt_2Cl_2(\mu\text{-}Me_2Ppy)_2]$ [90].



(58)

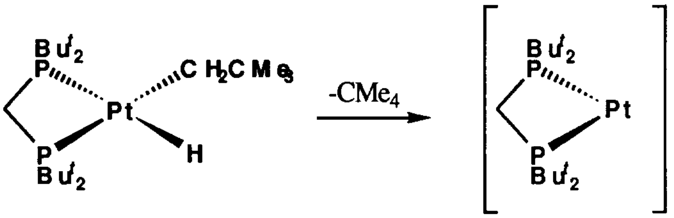
Treatment of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with an excess of NO^+A^- (A = BF_4, PF_6) leads to isolation of the stable cationic species $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]^+$. Reaction of the corresponding halogeno-complexes $[Pt_2X_2(\mu\text{-}dppm)_2]$ with $NOBF_4$ gave the analogous compounds $[Pt_2X_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]BF_4$ (X = Br, I). The crystal structure of $[Pt_2Cl_2(\mu\text{-}NO)(\mu\text{-}dppm)_2]^+$ was determined by an *X*-ray diffraction study, and confirmed the presence of an A-frame structure (**59**) [91]. Two-dimensional ^{31}P homonuclear shift correlated spectroscopy has been applied to the analysis of a series of dinuclear Pt(I) complexes containing phosphine ligands. On the basis of the spectra it was established that cross-peak positions of the Pt-P satellite signals can be used to determine the sign and magnitude of the $^2J_{Pt\text{-}P}$ coupling constant [92].



(59)

5.5 PLATINUM(0)

Cyclohexyneplatinum(0) complexes $[Pt(C_6H_8)L_2]$ (L = $PBu^t{}_2Ph$, PBu^tPh_2) have been prepared by reaction of the complexes $[PtL_2]$ with 1,2-dibromocyclohexane and 1% Na/Hg. The reactivity of the complexes with HCl, and with MeOH, in the presence and absence of O_2, was explored [93]. Reductive elimination of *neo*pentane from **(60)** at ambient temperature, generates the reactive 14-electron intermediate **(61)** *in situ* [94].



(60) **(61)**

The platinum(0) complex $[Pt\{P(OC_6H_4OMe\text{-}2)_3\}_3]$, containing the new ligand $P(OC_6H_4OMe\text{-}2)_3$, has been prepared by a variety of routes, including reduction of the corresponding dichloroplatinum(II) complex, or by ligand exchange reactions between the phosphite and $[Pt(\eta^2\text{-}C_2H_4)_3]$ or $[Pt(\eta^2\text{-norbornene})_3]$ [95]. The first *X*-ray structure for a platinum dibenzylideneacetone compound has been reported [96]. A convenient synthetic route for the production of platinum(0)-phosphine complexes has been described; the procedure involves reduction of platinum(II)-phosphine complexes using fluoride [97].

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