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4. **Palladium**

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CONTENTS

INTRODUCTION

The coordination chemistry of palladium reported during 1991 has been reviewed. The main source of information has been "CAS Selects:- Platinum and Palladium Chemistry" which has been

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surveyed up to issue 22, 1992. Compounds containing only palladium-carbon bonds, nonstoichiometric solid state complexes and alloys have been excluded. Complexes have been classified according to the oxidation state of the palladium and the nature of the ligand donor atoms. Where a complex contains mixed ligands or donor sets, it is treated under the donor atom nearest the top left of the periodic table. A separate section is included on the use of coordination chemistry to extract palladium.

A review of the chemistry of the platinum group metals has appeared [1]. Isomerisation of palladium(II) complexes has been reviewed in terms of the ligand trans effect [2].

4.1 PALLADIUM(IV)

The oxidation of sulphite and chloride complexes has been studied using various aqueous oxidants [3]. $[PdCl_6]^{2-}$ has been reacted with H_6TeO_6 in aqueous NaOH or KOH to give palladium(IV) telluride complexes [4]. The crystal structure of $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]$ has been determined. The palladium atom is coordinated octahedrally to six oxygen atoms. $[PdCl_6]^{2-}$ has also been reacted with $[IO_4]^{2-}$ in aqueous alkaline solution [5] to give $M_6[Pd(OH_2)(HIO_6)_2].nH_2O$ (M = Na or K).

The redox chemistry of some palladium chloro ammine complexes has been studied [6] and the redox potential of $[Pd(RNH_2)_2Cl_4]/[Pd(RNH_2)_2Cl_2]$ found to be 1.10 V (R = Me) and 1.11 V (R = Et). Oxidative addition of methyl iodide or benzyl bromide to [PdMePh(bpy)] gives the first arylpalladium(IV) complexes [PdXMePhR(bpy)] [7]. These decompose by reductive elimination of organic fragments to give ethane and toluene.

Mixed IV-II oxidation state complexes of palladium have been prepared using various tetradentate nitrogen ligands [8]. These have the formula $[PdL][PdLX_2]Z_4$ (X = Cl, Br; Z = BF_4, ClO_4 or PF_6) and have a linear chain structure. Their electronic properties were investigated. The crystal structure of another mixed oxidation state compound, $[PdL_2Br_2][PdL_2]Br_4$ (L = (–)-1,2-cyclohexanediamine) has also been reported [9]. Thermal decomposition of $(NH_4)_2[PdCl_6]$ occurs via the intermediate $(NH_4)_2[PdCl_4]$ [10]. The ^{35}Cl NQR spectrum of $[PdCl_6]^{2-}$ was investigated [11] and the $[NMe_4]^+$ salt found to be a clathrate, $[NMe_4]_2[PdCl_6].Cl_2$ whose crystal structure has been determined.

4.2 PALLADIUM(II)

4.2.1 Complexes with boron ligands

The reaction of $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ with $[B_3H_8]^-$ results [12] in substitution of the chloride ligands by $[B_3H_7]^{2-}$ for n =1-4. No reaction occurs with higher values of n as the starting compounds are dimeric with *trans* chloride ligands. The structure of the palladaborane

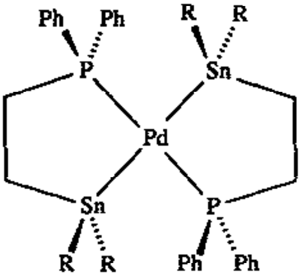
$[PhCH_2NMe_3]_2[(B_{10}H_{12})_2Pd]$ has been reported [13]. Phosphine migration from palladium to carborane takes place[14]:

$$[NMe_4][7\text{-}SR\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}] + Pd(PPh_3)_2Cl_2 \rightarrow PdPPh_3Cl[7\text{-}SR\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9] + C_6H_6 + [NMe_4]Cl$$

A similar reaction [15] with the [*nido*-7,8-$As_2B_9H_{10}]^-$ anion gives clusters with a $PdAs_2B_9$-core. Palladium(II) chloride has been reacted with a variety of *exo*-dithio-7,8-dicarba-*nido*-undecaborane derivatives to form $[MLCl_2]^-$, $[M_2L_2Cl_2]$ and $[ML_2]$ compounds [16].

4.2.2 Complexes with tin ligands

The complex $(PPh_3)_4Pd$ was reacted with $Ph_2PCH_2CH_2SnR_3$ (R = Ph, Me) to give a trans Pd(II) stannyl complex (**1**) [17].



(**1**)

The $[PdCl_{4-n}(SnCl_3)_n]$ system has been investigated spectrophotometrically in hydrochloric acid/water [18]. Stability constants were: log $K_3 = 4.41$, log $K_4 = 4.12$, log $K_5 = 3.88$. Oxidation occurs and Pd-Sn bonds are ruptured when $(Me_4N)_4[Pd(SnCl_3)_5Cl]$ reacts [19] with $[S_2O_3]^{2-}$ and $[SO_3]^{2-}$. Processes occurring in isopropyl alcohol [20] and nitromethane [21] solutions of palladium(II) tin chloro complexes have been investigated by ^{119}Sn NMR and Mössbauer spectroscopy.

4.2.3 Complexes with nitrogen ligands

4.2.3.1 Monodentate ligands

Patents have appeared for the manufacture of $Pd(NH_3)_2Cl_2$ [22], $[Pd(NH_3)_4]Cl_2$ [23] and $[Pd(NH_3)_4](HCO_3)_2$ [24]. The preparation of $[Pd(NH_3)_2C_2O_4]$ has been reported [25]. Patents have also appeared for the manufacture of $[Pd(NH_3)_2(NO_2)_2]$ [26, 27]. The crystal structure [28] of β-trans dichlorodiamminepalladium has been determined and the thermal decomposition [29] of $[Pd(NH_3)_2Cl_2]$ has been studied. The stability constants for $[Pd(NH_3)_m(H_2O)_{4-m}]^{2+}$ have been determined [30] as 9.56 ± 0.12, 8.87 ± 0.07, 7.52 ± 0.03 and 6.79 ± 0.03 for m = 1-4. The oxidation of palladium ammine thiosulphate complexes has also been studied [31].

The reaction of β-diketonatopalladium(II) with 4-substituted pyridines has been studied [32]. Reaction of $PdCl_2(PhCN)_2$ with 2,6-di-β-ketoester substituted pyridines (H_2Q) gave *trans* $Pd(H_2Q)_2Cl_2$ [33]. The ligand substituents formed *O-O*-chelates with Cu(II). The reaction of 1,4 substituted benzodiazepines with $Pd_2X_4(PPr_3)_2$ cleaves the halide bridge to give monomeric complexes [34]. The stability of the complex depends on the substituents with the 2-keto-form being less stable. The $[PdCl_6]^{2-}$ ion reacts [35] with creatinine (L) to give $[PdL_4]^{2-}$. The ligand aziridine of PdL_2Cl_2 reacts with NH_4Cl to form ligated 2-chloroethylamine. Similar reactions [36] occur with the $[PdL_4]^{2-}$ ion to give 2-aminoethylaziridine and *N*-(2-chloroethyl)ethylenediamine with HCl. The monodentate azide in $PdL(N_3)$ (HL = 2-(((2-diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate) reacts [37] with *p*-$MeOC_6H_4CN$ to give a tetrazole ligand $N_4CC_6H_4$-*p*-OMe bound through the N^2-atom.

Several palladium(II) amido complexes have been prepared and these include the compounds $(PPh_4)_2[Pd_2Cl_4(NH_2)_2]$, $PPh_4[PhC(NH_2)(NH)PdCl_3]$ [38], $(Me_3P)_2Pd(C_6H_4C(H)=NCHMe_2)(NHPh)$ [39] and $PdH(NHPh)L_2$ (L = $P(CHMe_2)_3$ or PCy_3) [40]. A number of PdL_2X_2 complexes have been prepared and are presented in Table 1.

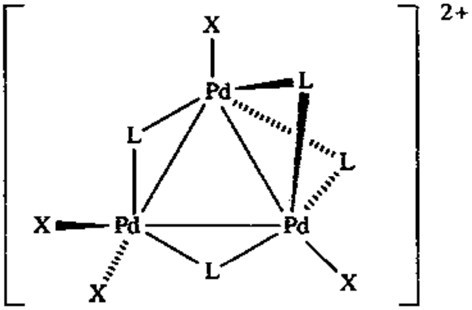
Table 1 ***PdL_2X_2 complexes with N-donor ligands***

L	X	Reference
4-vinylpyridine 1-vinylimidazole 4-methyl-5-vinyl-thiazole	Cl	[41]
2-pyrrolidone	Cl	[42]
2-methyl-5-vinyl-tetrazole	Cl	[43]
N-methylpiperazine	Cl	[44]
$NHEt_2$	dialkylcarbamato	[45]

4.2.3.2 *Bidentate ligands*

The IR spectra of dimethylglyoxime chelates of palladium have been measured [46] and hydrogen bond distances calculated. The kinetics of substitution of *N,N,N'N'*-R_4en (R = Me, Et) with chloride ion on palladium(II) have been studied [47]. The data support an associative mechanism. The intramolecular aromatic ring stacking has been studied by ^1H NMR spectroscopy in $Pd(L)(UTP)^{n-}$ (L = phen, bpy, n = 2; L = DL-tryptophan, n = 3; UTP = uridine 5-triphosphate) [48]. The degree of interaction is greatest for L = phen and least for L = DL-tryptophan. The cytotoxicity of $Pd(L)(XO_3)$ (L = bpy, phen, 2,2' dipyridylamine, en, ±*trans*-1,2-diaminocyclohexane; X = Se,Te) has been studied [49]. The tellurite complexes are more effective cell inhibitors than the selenite ones. The complex $[(en)Pd(4,4'\ bpy)]_4(NO_3)_8$ shows the ability to recognise aromatic compounds in D_2O [50].

In the palladium(II) complex $[PdL_2Cl]BF_4$ (L = 6-methyl-2,2'-bipyridine), one of the ligands is only monodentate with the nitrogen atom on the methyl substituted ring being uncoordinated [51]. Several complexes of palladium(II) with 1-methylcytosine have been prepared [52]. This ligand can also be either mono or bidentate. In the complex $(PPh_3)_2PtLPdCl_2$ (L = 1,10 phenanthroline-5,6 dithiolate) the ligand bridges the two metal atoms [53] and bonds to the palladium atom as a bpy type ligand. Bidentate nitrogen ligands also act as bridging groups in $[Pd_3L_4X_4]X_2.nH_2O$ (X = Cl, n =3; X = Br, n = 2; L = 3,5-diamino-1,2,4-triazole) [54] which has the structure shown in (2).



(2)

A pyrazolate ligand has been used to bridge between palladium and rhodium in the heterometallic complex $Pd\{Rh(\mu\text{-}pz)(\mu\text{-}SCMe_3)L_2\}_2$ where L_2 = COD, $(CO)_2$, $CO(PPh_3)$, or $CO(P(OMe)_3$ [55].

A number of $PdLX_2$ complexes have been prepared and these are listed in Table 2. A range of complexes of general type PdL_2 has also been prepared and the compounds are given in Table 3.

Table 2: Some $PdLX_2$ complexes

L	X	Reference
Dimethylaminoferrocene	Cl	[56]
2-(2-*N*,*N*-di-2,2-propenyl aminoethyl)pyridine	Cl	[57]
2,2'-biquinoline	Cl, Br	[58]
2,2'-bipyridine	Cl	[59]
phen bpy	succinamide	[60]
morpholinobiguanide piperidinobiguanide	halide, thiocyanate, hydroxide	[61]
3,3', 5,5', and 7,7'-dimethyl-2,2'-diindazole	Cl, Br, C_6F_5	[62]
en	isopropylphosphonato	[63]

Table 3: Some PdL_2 complexes.

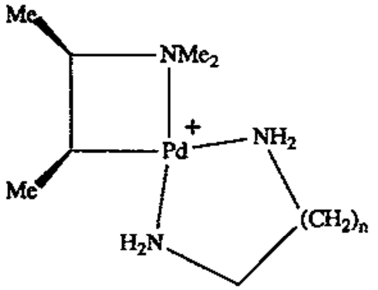
L	Reference
4,4'-diisocyanobiphenyl	[64]
R:C(Me)C(CO_2Et):NOH (R = H, Me, Et, Pr, Bu, CH_2Ph)	[65]
2,3-bis(hydroxyimino)-1,2,3,4-tetrahydro-pyrido[2,3b]pyrazine	[66]
3,5-R-pyrazole 3,5-R-1-methyl-pyrazole (R = NCO, N$(CN)_2$, C$(CN)_3$)	[67]

4.2.3.3 Carbon and nitrogen bidentate ligands

There is a large number of complexes where the ligand is bonded through both carbon and nitrogen. In many of these, the ligand has undergone orthometallation. With *N,N'*-diarylformamidines and *N,N'*-diarylacetamidines $[PdCl_4]^{2-}$ reacts [68] to form a six membered metallocycle whereas with *N,N'*-diarylbenzamidine a five membered metallocycle is formed. These $[PdLCl]_n$ complexes can be cleaved by a variety of monodentate ligands. 2-phenylpyridine can give either monodentate *N*-bonded complexes or cyclometallated ones depending on the reaction conditions [69]. A four membered metallocycle ring, (3), has been prepared [70].

The agostic interaction of pendant C-H substituents on cyclopalladated complexes has been studied [71] using phase sensitive ^1H 2D NOESY. The C-H bond lies above the square plane of the complex. Alkyne fragments have been inserted [72] into the Pd-C bond in (4).

Cyclometallating ligands can also be used to bridge between metal atoms. The complexes $Pd_2Y(H_2O)_3Cl$ and $PtPd(YH_2)(H_2O)_2Cl_2$ (YH_3 = 4,6-diphenyl-5-phenoxy-1,2-dihydropyrrimidine-2-one) have been prepared [73] and the water ligands replaced by en and py. A cyclopalladated polymer (5) has been prepared [74].



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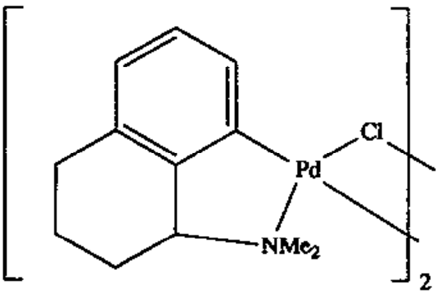

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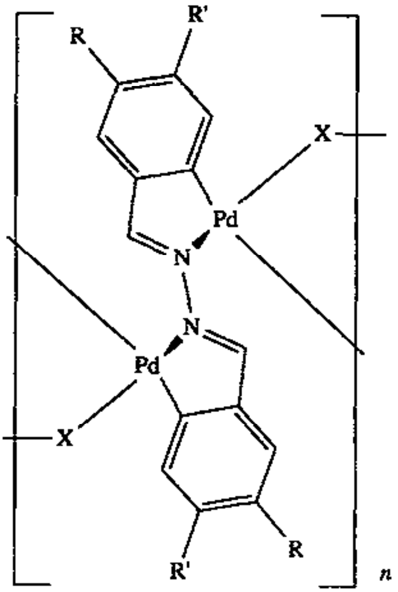
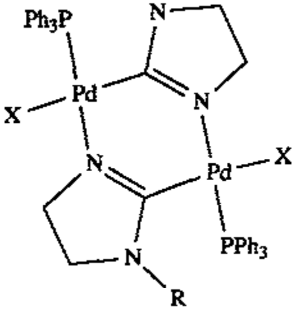


R =R' = MeO, R = R' = OCH_2O; X = Cl, OAc

(5)

Other ligands can also give bridges in cyclometallated complexes. Palladium(II) acetate reacts with *N*-(3-methoxy)benzylidenecyclohexylamine to give an acetato-bridged dimer. The acetato bridge can be replaced by halides and then dppm or $Ph_2PC(=CH_2)PPh_2$ to give a dimer with a halide and a diphosphine bridging [75]. A complex has been prepared [76] where the ligand bridges through both C and N atoms (6) (R = Me, 4-$MeOC_6H_4$; X = Br, Cl).



(6)

Table 4 Cyclopalladated complexes of general type $[PdLX_2]_n$

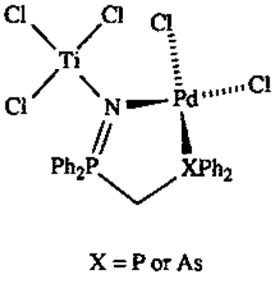
L	X	n	Reference
2',6'-dimethylazobenzenato	μ-chloro	2	[77]
N-(3-methoxybenzylidene)- and *N*-(4-methoxybenzylidene)-cyclohexylamine; *N*-(4-methoxybenzylidene)-2,4,6-trimethylaniline	μ-acetato μ-halide PPh_3, PBu_3, PCy_3	2 2 1	[78]
dimethylbenzylamine 8-quinolylmethyl	C_6F_5 & NCMe, PPh_3, $PPhMe_2$, Br C_6F_5 & μ-Br	1 2	[79]
N,N'-diethyl-2,6-dialdiminobenzene	μ-Cl NCMe & ClO_4 py, bpy, various donor ligands	4 2	[80]
1-methyl-2,2'-bipyridin-3-ylium	NO_3, H_2O	1	[81]
4-hydroxy-4'-methylazobenzene	μ-Cl	2	[82]
N,N'-di-R-benzene-1,3-dicarbaldimines. R = Et, Bu, octyl, benzyl	μ-acetato μ-Cl various donor ligands	4 4 2	[83]
N-(3,4-dimethoxybenzylidene) cyclohexylamine	μ-Cl, Br, I	2	[84]
4'-(methoxyphenyl-NNO-azoxy-N2)-4-methoxyphenyl-2-ato	μ-Cl salicylideneaniline	2 1	[85]

Dioximes of 1,3 and 1,4 diacetylbenzene undergo double cyclopalladation to bridge two palladium atoms. 1,5 bis(dimethylamino)naphthalene can be singly and doubly cyclopalladated [86].

A number of other cyclopalladated complexes of general type $[PdLX_2]_n$ have been prepared and are listed in Table 4.

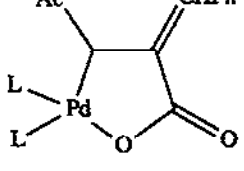
4.2.3.4 Complexes with nitrogen and oxygen or phosphorus donors

The bimetallic titanium-palladium complex (7) can be made [87] with the nitrogen-phosphine or arsine ligand starting on either the titanium or palladium atom (X = P, As).



(7)

The thermal decomposition of PdL_2 (HL = 2-hydroxy-4-n-propoxyacetophenone oxime) has been studied [88]. Palladium(II) complexes of 2,3-disubstituted quinazolin-(3*H*)-4-ones have been prepared and their thermal analysis [89] shows loss of ligand. Complexes of palladium(II) with 2-aminonicotinaldehyde acetylhydrazone and phenylacetylhydrazone have been prepared [90] and the ligand found to be bidentate. When phen reacts [91] with $Pd(HL\bullet)_2$, (H_2L = $Me_2C(N{=}O)C(Me){=}NOH$) an intermediate radical is formed: $[Pd(phen)(HL\bullet^-)]$. The reaction of $Pd(Ph_2P(CH_2)_3PPh_2)Cl_2$ with α-acetamidocinnamic acid and silver(I) oxide gives (8) whereas the reaction [92] of PdL_2Cl_2 (L = PPh_3, $PMePh_2$, PMe_2Ph, L_2 = $Ph_2P(CH_2)_4PPh_2$ with 2-acetamidoacrylic acid gives (9).



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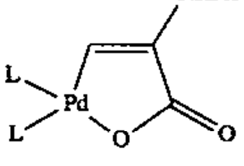


(9)

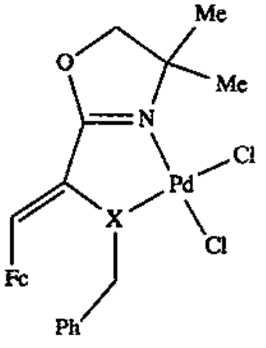
The complexation of palladium with aliphatic amino acids has been studied [93]. The stability is dependent on the aliphatic chain length. In PdL_2X_2 (L = diethyl-2-quinolylmethylphosphonate, X = Cl, Br) the ligand is monodentate but in *cis* $PdLX_2$ it is bidentate, bonding through nitrogen and oxygen atoms [94]. The complexes have been screened for antitumor properties but only PdL_2Br_2 shows activity. A PdL_2 complex has been obtained [95] for HL = L-citrulline which from spectroscopic evidence contains ligand bonded through carboxylic acid and amine groups. The complexes $[PdClL(\mu\text{-}Cl)]_2$ and $PdCl_2L_2$ (L = 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine) have been formed [96] from $PdCl_2(PhCN)_2$ and L. The corresponding bromo complexes have also been prepared. PdL_2 complexes have been prepared where L = substituted triazene-1-oxide [97].

The thermal decomposition of PdL_2 (L = fluorenone thiosemicarbazone [98], thiophene-2-carboxaldehyde thiosemicarbazone [99]) has been studied. The stability constants of palladium(II)-*N*-acyl-thiourea complexes have been determined and compared with those for Au(III) and Hg(II) [100]. The interaction of PdL_2 (L = 8-mercaptooxinate) with donor solvents has been studied [101].

The ligand pyramidine-2-thione acts as a monodentate *S*-bonded ligand to palladium(II) in acid media or methanol but in neutral or basic media also bonds through the ring nitrogen atom [102]. Similarly, reaction [103] of palladium(II) with aromatic thiosemicarbazide derivatives gives a variety of complexes where the ligands can be bidentate or bridging tetradentate. Mixed ligand complexes of palladium with methionine (bonded through amino nitrogen and sulphur atoms) and pyrimidine ligands have been prepared [104] and found to have antimicrobial activity. The complex $PdLCl_2$ (L = 6-ethoxybenzothiazole-2-sulfonamide) has been prepared and found [105] to be a strong inhibitor of red cell bovine carbonic anhydrase.

The technique of NMR spectroscopy has been used to examine [106] PdL_2 (L = parasubstituted *N,N*-diallyl-*N'*-benzoyl-thiourea) and the thiocarbonyl carbon atom has been assigned using ^{195}Pt-^{13}C coupling satellites. The complex $Pd_2L_2Cl_2(PMe_3)_2$ (HL = pyridine-2-thiol) has been studied [107] using a variety of NMR spectroscopy techniques.

A new ferrocenyl derivative has been prepared [108] and complexes with palladium(II) to give (**10**). The complex has non-linear optical properties.



X = S, SO

Fc = ferrocenyl

(**10**)

In addition, $PdLCl_2$ complexes have been prepared and characterised for L = *N,N*-diethyl-2-octylthioacetamide [109], 2-mercaptopyrimidine and 2-thiocytosine [110]. PdL_2 (L = 4-amino-3-mercapto-1,2,4-triazole) has been prepared [111] and Pd_2L_2 (H_2L = 2-(2-mercaptophenyl)imino-4-pentanone) has been prepared *in situ* [112] from 2,4-pentanedione, 2-aminobenzenethiol and palladium(II). Complexes with bridging S_2N_2 and $[S_3N_2]^{2-}$ ligands have been prepared [113] by the reaction of S_4N_4 with $[Pd_2Cl_6]^{2-}$. The crystal structures of PdL_2 complexes with *S,N*-chelates have been determined for L = thiophene-2-carboxaldehyde-4-phenylthiosemicarbazonato [114] and 1-isopropyl-3-methyl-4-cyclohexylaldimine-5-thiopyrazolato [115]. The latter is unusual in that the sulphur atoms are *trans* to each other.

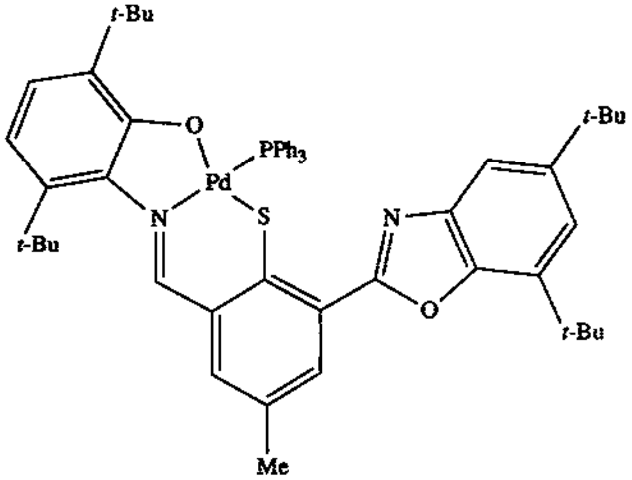
4.2.3.5 Terdentate nitrogen ligands

The reaction of binary and ternary diethylenetriamine(dien) palladium complexes with other amines has been investigated [116]. The binding of $[Pd(dien)]^{2+}$ with 8-azapurines and 7-deaza-8-azapurines has been studied [117] using ^1H NMR spectroscopy. The terdentate ligand complexes PdLCl have been prepared [118] by the condensation of isonitrosoenzoylacetone and either ethylenediamine or trimethylenediamine in the presence of palladium(II). The complex $[PdLCl]^+$ has been prepared [119] for L = 2,6-di(benzimidazol-2-yl)pyridine and other derivatives. The potentially pentadentate ligand *N,N'*-di(2-picolyl)-*N*-(2-pyridinecarboxamide)-1,2-diaminocyclohexane coordinates [120] to palladium as a terdentate ligand through the two picolyl pyridine nitrogen atoms and the secondary amine group.

4.2.3.6 Terdentate ligands with nitrogen and other donor atoms

The binding of the terdentate ligand 2,6-bis(methylthiomethyl)pyridine has been studied [121] by potentiometric and spectrophotometric techniques. Its acidity constant was $\log K = 4.04 \pm 0.04$. The rate of substitution of the chloride ligand in PdLCl (L = *N*-(3-dimethylamino-1-propyl)salicylaldimine) has been studied [122] and an associative mechanism is supported. The ligand pyridine-2,6-dicarboxylic acid becomes [123] terdentate rather than bidentate on raising the pH from 1.4 to 5 giving $[PdLCl]^-$. Similarly MeC(=NOR)C(Me)=NNHCSR' (H_2L; R = H, R' = NH_2, NHPh, SMe; R = Me, R' = NH_2, SMe) reacts with $[PdCl_4]^{2-}$ to give bidentate complexes initially (bonded through S and hydrazinic N) [124]. On reaction with amines these complexes give PdLA (A = amine) where L is bonded through *O, S*- and hydrazinic *N*-donor sets. The complex (**11**) has been obtained [125] by the oxidation of one ligand side arm to a benzoxazole.

The reaction [126] of PdLCl (L = cyclometallated 2'-benzylthio-4-methylazobenzene) with chlorine results in formation of chlorinated azobenzenes rather than palladium oxidation. Palladium(II) ion reacts with *N*-phenylsulfonyl- and *N*-(tosyl)-glycine to give tetrameric complexes [127] $Pd_4(\mu\text{-}Cl)_2L_4$ where two ligands are cyclometallated to become terdentate (*O,N,C*) and another two act as bridging carboxylates. The palladium ions are bridged by chloride and carboxylate groups. Terdentate *O,N,C*-ligands have also been prepared using 2-substituted 8-quinolinols [128]. The substituent side-chain provides a carbanion to form a Pd-C bond. The luminescence spectrum of Pd(2,6-diphenylpyridine)py has been recorded [129] and involves the terdentate ligand although electrochemical results suggest that the LUMO is centred on the metal atom. Reaction of 6-(2-thienyl)-2,2'-bipyridine with $[PdCl_4]^{2-}$ gives a cyclometallated *N,N,C*-complex PdLCl [130].



(11)

4.2.3.7 *Tetradentate nitrogen ligands*

The association in solution of PdL (L = 6-t-Bu-2,3-naphthalocyanine [131], tetra(*p*-sulfophenyl)porphine and tetra(4-*N*-methylpyridyl)porphine [132]) has been studied. A complex of 3,5-pyrazoledicarboxylic acid has been prepared [133] where the ligand coordinates as the trianion giving $[Pd_2L_2]^{2-}$. A six-membered ring of four nitrogen atoms and two palladium ones is formed. Other PdL complexes are listed in Table 4.

4.2.3.8 *Other multidentate N-containing ligands*

The binding of edta with palladium(II) has been studied [134] spectrophotometrically at pH 0.5-7.5. PdL (H_2L = bis(salicylidene)-o-phenylenediamine) has been prepared [135]. Electrolysis of this and other complexes [136] (H_2L = bis(acetylacetone)ethylenediamine, bis(salicylaldehyde)ethylenediamine) gave partially oxidised polymers. PdL complexes have also been prepared [137] for H_2L = 6,6-dimethyl-5,7-dioxo-1,11-dithia-4,8-diazacyclotetradecane and 12,12-dimethyl-11,13-dioxo-1,4,7-trithia-10,14-diazacyclohexadecane.

The crystal structure of [PdL]NCS (HL = 1-phenyl-3-{2-[(2-aminoethyl)-amino]ethylimino}-1-buten-1-ol) has been determined [138] and the palladium atom is coordinated by a distorted N_3O-square set of donor atoms. Complexes Pd_2LBr_4 with L = [18]aneN_6 and [20]aneN_6 have been prepared and structurally characterised [139]. Two palladium(II) ions each coordinate to three of the nitrogen atoms and the remaining coordination site is occupied by a bromine atom. The Pd-Br bonds are mutually *trans* in the [18]aneN_6 complex but *cis* in the [20]aneN_6 one.

Table 4: Complexes PdL with tetradentate nitrogen ligands

L	Reference
5-amino-2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin 5-(4-isothiocyanotobenzamido)-2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin	[140]
2,3,7,8,12,13,17,18-octaethylporphyrin, octaethylchlorin, octaethylisobacteriochlorin	[141]
meso-diphenyltetrabenzoporphyrin	[142]
1,8,9,20-tetrahydro-3,6,9-trimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[3,4-f:4',3'-j][1,2,5,8,9,12]-hexaazacyclotetradecine	[143]
tetraaza[14]annulenetetracarbonitrile	[144]
N,N'-bis(2-pyridinecarboxamide)-1,2-diphenylethane *N,N'*-bis(2-pyridinecarboxamide)phenylethane	[145]
N,N'-bis(aminoalkyl)oxamides	[146]

4.2.4 Complexes with phosphorus and arsenic ligands

4.2.4.1 Monodentate ligands

Infrared spectral data for $Pd(PR_3)SO_2$ have been reported [147]. PdL_2Cl_2 complexes have been prepared with several novel phosphine ligands; L = 4,6-R_2-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [148], 10-phenylphenoxaphosphine and *N*-methyl-*P*-

methylphenophosphazine [149], and $(cyclopentyl)_nPPh_{3-n}$; n = 1-3 [150]. The crystal structure of *trans* $PdI_2(PPh_3)_2.HCCl_3$ has been reported [151].

The complex $PdCl_2(PPh_3)_2$ has been reacted [152] with 8-hydroxyquinoline, oxalate and salicylaldehyde to give complexes where the chloride ligands are replaced by the bis-chelates. Similarly, *trans*-$Pd(PPh_3)_2(thiourea)_2$ has been prepared [153] by the reaction of thiourea with the corresponding chloro complex. The pyridine ligand in *trans*-$PdCl(C_5H_4N\text{-}C^2)(PMe_2Ph)_2$ has been protonated [154] with $HClO_4$ to give a 2-pyridylium ligand. Reaction of $Pd(PR_3)_2$ with acids $[H_3O^+]X$ (X = BF_4, BF_3OH) leads to hydride complexes *trans*-$[Pd(PR_3)_2(H)(H_2O)]X$ (R = tert-Bu [155], cyclohexyl [156]. However when $[Pd(OAc)_2(PPh_3)]_2$ reacts [157] with formic acid the phosphine ligand is oxidised and a phenyl group is transferred to the palladium atom to give $[Pd(\mu\text{-}O_2PPh_2)Ph(PPh_3)]_2$.

The crystal structure of *trans*-$PdEt(SPh)(PMe_3)_2$ has been reported and its reaction with CO studied [158]. Insertion initially takes place in the Pd-C bond. The reaction [159] of $Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$ with L = thietane gives $PdCl_2(PMe_3)L$ under mild conditions but with more severe conditions the ring is opened to give $Pd_2Cl_2(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}Cl)(PMe_3)_2$. A number of dipalladium thiolato complexes have been prepared, including *cis*-$Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SR)(PMe_3)_2$ (R = Me, CMe_3, Ph), and *trans*-$Pd_2Cl(\mu\text{-}SPh)_2(PR_3)_2$ (R = Et, Me) [160].

A number of palladium-sulphur clusters containing phosphine ligands have been prepared. These are summarised in Table 5.

Complexes of bidentate arsenic ligands (L = $PhAsRCH_2(CH_2OCH_2)_nCH_2AsRPh$; R = Me, Et, Pr, Bu; n = 1,2) with $[PdCl_4]^{2-}$ have been prepared [161].

Table 5: Palladium-sulphur clusters containing phosphine ligands.

Cluster	Reference
$[Pd_3S_2(dppe)_3][PF_6]$	[162]
$Pd_3Se_2(SeSiMe_3)_2(PPh_3)_4$, $Pd_5Se_5(PPh_3)_5$, $Pd_8Se_8(PPh_3)_8$, $Pd_6Se_4Cl_4(PPh_3)_6$, $[Pd_8Se_8Cl(PPh_3)_8][CpCrCl_3]$, $Pd_5Se_4Cl_2(PPh_3)_6$, $Pd_7Se_6(SeH)Cl(PPh_3)_7$, $Pd_6Se_4(SeH)_2Cl_2(PPh_3)_6$, $Pd_6Se_4(SeH)_4(PPh_3)_6$, $Pd_4NiS_4Cl_2(PPh_3)_6$	[163]
$Pd_3(\mu\text{-}SCy)_4Cl_2(PMe_3)_2$	[164]

4.2.4.2 Complexes with multidentate phosphorus ligands

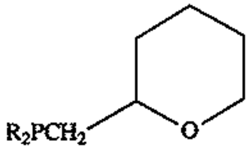
The reaction:

$$\mathrm{Pd(dmpe)Me_2 + [HNRR'R'']X \rightarrow [Pd(dmpe)Me(NRR'R'')]X + CH_4}$$

has been carried out for a variety of amines [165]. The binding constants have been determined from ^{31}P NMR spectroscopic data. The mass spectral fragmentation of palladium complexes of diphenylphosphinoacetone has been studied [166] and can be useful in establishing whether a phosphinoenolate bis-chelate is present.

A number of novel phosphines have been synthesised and coordinated to palladium. The phosphine NIPHOS (NIPHOS= 2-(2-pyridyl)-4,5-dimethylphosphinine) has been complexed in $[\mathrm{PdCl(NIPHOS)PMe_3}]^+$ and adds water or methanol at the P-C6 double bond [167]. The ligand (*R,R*)-(*S,S*)-2,2''-bis[1-(diphenylphosphino)ethyl]-1,1'-biferrocene has been synthesised [168] and chelates to palladium in a *trans* orientation. The chelating ligand $\mathrm{H_2L}$ = 1,3-$\mathrm{(Ph_2PCH_2CO)_2C_6H_3}$ has been synthesised and complexed as a bridging ligand in $[(o\text{-}\mathrm{C_6H_4CH_2NMe_2)PdCl]_2(\mu\text{-}LH_2)}$ [169]. This can be converted into $[(o\text{-}\mathrm{C_6H_4CH_2NMe_2)Pd]_2(\mu\text{-}L)}$ by treatment with sodium hydride. The ligand reacts with $\mathrm{Pd(acac)_2}$ to give a polymer.

The potentially bidentate ligands (**12**) have been synthesized and monodentate $\mathrm{PdL_2Cl_2}$ complexes prepared [170]. Reaction of this complex with silver perchlorate gives *trans*-$[\mathrm{PdL_2Cl}]^+$ in which one ligand is *O,P*-coordinated.



R = Ph, c-$\mathrm{C_6H_{11}}$, Pr

(12)

Similarly, cyclometallation of (**13**) makes it a tridentate ligand and the crystal structure of PdLCl has been determined [171].

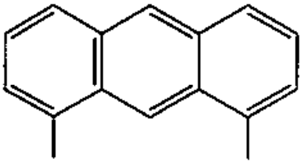


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Table 6: Palladium(II) complexes with multidentate phosphorus ligands

Complex	Reference
Pd(*cis*-1,5-diphenyl-1,5-diphosphacyclooctane)Cl$_2$	[172]
PdCl$_2$(dppf).0.5(CH$_3$)$_2$CO	[173]
Cl(C,P-tertbutylphosphino)(AsPh$_3$)Pd	[174]
cis-PdL$_2$X$_2$; L = 1-(thiomethyl)-2-diphenylarsino)ethane, 1-(thiomethyl)-2-diphenylphosphino)ethane; X = Cl, Me *trans*-PdL$_2$X$_2$; L = diphenyl(2-phenylethyl)phosp hine, diphenyl(1-naphthyl)phosphine, N-methyl-2-thiophenealdimine; X = Cl, Me	[175]
[PdCl$_2$(μ-Me$_2$PCH$_2$PMe$_2$)]$_2$	[176]
Pd$_2$(dppm)$_2$(CN)$_4$	[177]
PdCl$_2$(R,R'-2,2"-bis(diphenylphosphino)-1,1"-biferrocene)	[178]

Table 7: Bridging modes adopted by multidentate phosphorus ligands

Complex	Reference
[(Me$_3$CNC)$_2$RhCl$_2$(μ-Ph$_2$Ppy)Pd(μ-Cl)]$_2$, (COD)Rh(μ-Cl)(μ-Ph$_2$Ppy)PdCl$_2$	[179]
Fe{Si(OMe)$_3$}(CO)$_3$(μ-dppm)Pd(_3-2-RC$_3$H$_4$); R = H, Me Fe{μ-Si(OMe)$_2$OMe}(CO)$_3$(μ-dppm)Pd(SnPh$_3$)	[180]
trans-(NC)$_2$Pd(μ-dppm)$_2$AgX; X = NO$_3$, NO$_2$, OAc, OOCH	[181]
PdM$_2$(Cp)$_2$(CO)$_5$(μ-dppm), [Pd(μ-CO)(μ-dppm)$_2$M(Cp)(CO)]$^+$; M = Mo, W	[182]
NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$	[183]
Pd$_2$(O$_2$CR){μ-C$_2$(CO$_2$Me)$_2$}(μ-Ph$_2$PCH$_2$SCH$_2$Ph)$_2$; R = Me, Ph, HMePh	[184]

A number of other palladium phosphine complexes have been prepared and are summarised in Table 6.

Multidentate phosphine ligands can also bridge between metal ions and a number of mixed metal compounds utilise this feature. Those prepared recently are summarised in Table 7.

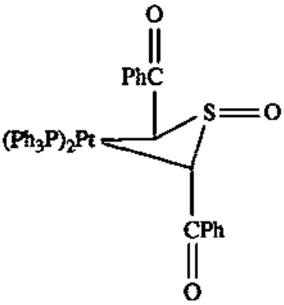
There has also been some work on the reactivity of palladium phosphine complexes. Reaction of PhOH with $PdMe_2L$ (L = 1,2-bis(dimethylphosphino)ethane) gives PdMe(OPh)L [38]. $Pd_2Cl_2(\mu\text{-}Ph_2P\text{-}2\text{-pyridyl})$ reacts with $(Ph_2P)_2CHMe$) to give substitution of the phosphine ligand [185]. This complex can then react with X = CO, SO_2, H_2S to give complexes where these groups also act as bridging ligands. Carbonylation of $[Pd(dppm)(OOCCF_3)]_2$ gives $[Pd(dppm)(OOCCF_3)]_2(\mu\text{-CO})$ [186]. Reaction of $PdLCl_2$ (L = 1,3-bis(diisopropylphosphino)-propane) with $LiBEt_3H$ gave [187] the hydride bridged compound $[LPd]_2(\mu\text{-H})_2.LiBEt_4$. Similarly, LPd(Ph)Cl reacted with methanol and NEt_3 to give $(PdL)_2(\mu\text{-H})(\mu\text{-CO})$ [188]. The complexes $PdL(C_2H_4)$ (L = chelating diphosphine) have been protonated to give $[PdL(C_2H_5)]^+$, which contains an agostic hydrogen atom [189]. The palladium complex $[(dppp)Pd(Ac)(NCMe)]^+$ has been reacted with a variety of alkenes to give alkene insertion into the acetyl group [190].

4.2.5 Complexes with oxygen ligands

A patent has appeared for the manufacture of chloride-free palladium oxide [191]. The heat of isomerisation of palladium(II) acetylacetonoate has been determined [192] and its ionization with various reagent gases has been studied [193]. The thermal decomposition of $PdL_2.2H_2O$ has been studied for HL = isoorotic and 2-thioisoorotic acid [194].

The complexation of $[PdCl_4]^{2-}$ and 3,6-dithiaoctane-1,8-diol has been studied spectrophotometrically [195] and 1:1 and 1:2 complexes found. Palladium(II) diacetylacetonoate has been reacted [196] with PhNNCl to give $Pd(3\text{-PhNN-acac})_2$.

The platinum complex (**14**) reacts with $PdCl_2(NCPh)_2$ to give a complex where it acts as a bidentate ligand bonding through sulphur and carbonyl oxygen to PdCl [197].



(14)

A series of $Pd(PPh_3)(Me)L$ complexes have been prepared [198] where L is a substituted *β*-diketonate or monothio-*β*-diketonate ligand.

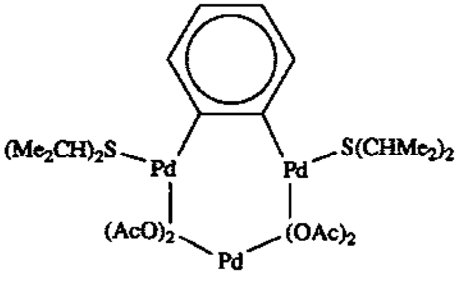
Some alkali metal palladates $M[Pd(OH)_4]$ (M = Ca, Sr, Ba) have been prepared in 4-8 M NaOH solution but in concentrated solution, $Sr_4Pd(OH)_{10}$ is formed [199]. A complex with a bridging hydroxy ligand, $[NBu_4]_2[Pd(C_6F_3H_2)_2(\mu\text{-}OH)]_2$ has been prepared and reacted with a variety of other ligands to give substitution of the hydroxy bridge [200]. A number of other palladium complexes with oxygen donor atoms have been synthesised and are summarised in Table 8.

Table 8: Selected palladium(II) complexes with oxygen donor ligands

Complex	Reference
$Pd(NO_3)_2(H_2O)_2$	[201]
$[Ph_4As]_2$[(1,2-dithiooxalato)$_2$Pd]	[202]
Pd(8-quinolinol-*N*-oxide)$_2$, Pd(5,7,-dinitro-8-quinolinol-*N*-oxide)$_2$	[203]
$[MCl(L)]_2$; HL = (2-hydroxy-5-methylphenyl)aryltelluride; aryl = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$	[204]

The dimethylglyoximate ligand has been used to bridge between palladium and copper to form a Cu_2Pd complex species [205].

Reaction of palladium(II) acetate with $(Me_2CH)_2S$ in benzene gives [206] an unusual trinuclear compound (**15**). The palladium(II) acetate $(Me_2CH)_2S$ system has also been studied as an activator of aromatic C-H bonds in methyl-substituted benzenes [207].



(**15**)

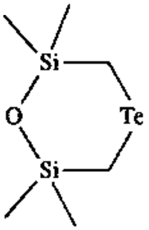
The mode of attack of acetate on *cis* and *trans* [5-carbomethoxy-(1,2,3-η^3)-cyclohexenyl)Pd(OAc)]$_2$ has been studied [208] and is external for the *cis* isomer but internal for the *trans* one. The thermolysis [209] of $Pd_4(\mu\text{-}L)_4(\mu\text{-}O_2CR)_4$ (L = CPh_2, CO; R = Me, CMe_3, Ph, CH_2Cl) in benzene or toluene led to oxygen transfer from the carboxylate to L and CO_2 insertion into the solvent in the case of L = CO. The carbonyl ligands in $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$ have been substituted[210 by diphenylcarbene groups.

4.2.6 Complexes with sulphur, selenium and tellurium ligands

A number of compounds containing palladium and chalcogen groups have been prepared. The crystal structures of $Pd_8(S_2)_4Cl_8$ [211], PdS_2Cl_6, $PdSe_2Cl_6$, $PdTe_2Cl_{10}$ [212] and $[PPh_4]_2[Pd(Te_4)_2]$.DMF [213] have been determined and the thermal decomposition [214] of PdS_2Cl_6 and $PdSe_2Cl_6$ found to give $PdCl_2$.

4.2.6.1 Monodentate ligands

The thermal decomposition of a series of palladium(II) chloride complexes with $RSOPhCH_3$ and $RSPhCH_3$ ligands has been studied [215] and found to depend on the alkyl group R. Some new PdL_2X_2 (X = Cl, Br) complexes have been prepared with L = 2-thiocoumarin [216], telluracyclopentane, telluracyclohexane, benzotelluracyclopentane [217] and (**16**) [218].



(**16**)

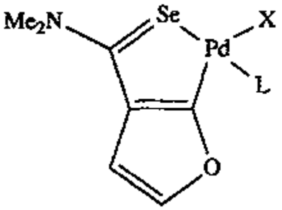
The complexes $(NBu_4)_2[Pd(SC_6F_5)_4]$, $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(C_6F_5)_2]_2$ and $(NBu_4)_2[Pd(\mu\text{-}SC_6F_5)(SC_6F_5)_2]_2$ have been obtained [219] by reacting $Tl(SC_6F_5)$ with palladium(II) halide complexes. The sulphur atom is also bridging in $[Pd_2(SPh)_6]^{2-}$ which contains two bridging ligands and four terminal ones [220]. A polymeric compound $[Pd(SR)_2]_n$ has been obtained [221] for R = C_6F_5, *p*-C_6HF_4 and *p*-C_6H_4F. The crystal structure of (18-crown-6)$K[Pd(SCN)_4].H_2O$ has been determined [222] and shows interaction between the K^+ ion and thiocyanate groups.

4.2.6.2 *Bidentate ligands*

The new ligand HL = $CH_2CH_2TeHC_6H_4R$-4 (R = MeO, EtO) has been synthesised and found [223] to coordinate to palladium via both tellurium and oxygen to give a $[PdClL]_2$ complex. DL-selenamethionine also chelates through selenium in $(SeMet)PdCl_2$ [224]. The bidentate ligand L = $(PhCH_2S)_2CH_2$ forms a number of complexes with palladium(II) in which it can function either as a bridging or chelating ligand depending on the stoichiometry [225]. The ligand 1,5-dithiacyclooctane functions as a chelating ligand to palladium(II) and the kinetics of its substitution with bipy and phen have been investigated [226]. The reaction is first order in both palladium(II) and the incoming ligand; an associative mechanism is indicated.

Several $[PdL_2]^{2+}$ complexes have been prepared. When L = 1,3-dithiepin-2-carbodithiolate the dithiepin ring acts as a π-acceptor [227]. The kinetics of ligand substitution have been studied by ^1H NMR spectroscopy for L = 1,4-dithiane and an associative mechanism is again favoured [228]. The electronic and magnetic properties of $[PdL_2]^{2+}$ salts are of interest. For L = bis(trifluoromethyl)ethylenedithiolate, the $[Mn(C_5Me_5)_2]^+$ salt is a metamagnet [229]. For L = 1,3-dithio-2-thione-4,5-dithiol, the 2-(1,3-dithiol-2-ylidene)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin salt is a molecular magnet down to at least 4K [230]. The optical properties of palladium compounds containing this ligand have also been investigated [231]. A complex has been prepared where the dithiocarbamate ligand bridges between palladium and zinc [232].

A number of complexes with chalcogen donor atoms are also cyclometallated. The reaction of $PdCl_2$ with *N*-thiopivaloyl pyrrolidine gives a chloro-bridged dimer where each palladium atom is coordinated to a ligand via both the sulphur atom and a carbon of the pyrollidine ring [233]. The ligand *N,N*-dimethylferrocenecarbothioamide bonds to palladium via the sulphur atom and one carbon of the cyclopentadienyl ring [234]. A selenium cyclopalladated complex, (**17**) (X = Cl, I; L = PBu_3, 4-tert-butylpyridine) has also been prepared [235].



(**17**)

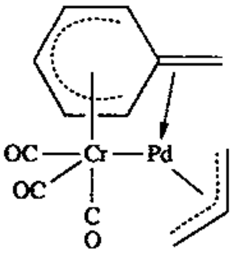
4.2.6.3 *Multidentate ligands*

The reaction of $PdCl_2(PhCN)_2$ with 2,2-dimethyl-3-butyn-1-ylmethylsulfide gives as a major product [7(Z)-chloromethylene-4,4,8,8-tetramethyl-2,10,dithiaundec-5(Z)-en-5-yl-*S,S*]PdCl where the palladium is coordinated to two sulphur atoms and one carbon atom [236]. Reaction of palladium(II) with 1,4,7-trithiacyclodecane gives [237] a 2:1 compound where each ligand is attached via two of its three sulphur donor atoms. Similarly, the potentially tridentate ligands L = 2,5,8-trithia[9]-*o*-benzenophane and 2,5,8-trithia[9]-*m*-benzenophane react [238] with $PdCl_2(PhCN)_2$ to give $PdCl_2L$. In both cases the extra sulphur donors are thought to interact with the palladium atom slightly.

4.2.7 Complexes with halide ligands

The far IR reflectance spectrum of K_2PdCl_4 and $(NH_4)_2PdCl_4$ has been determined at room temperature and 145 K [239]. Several $[PdCl_4]^{2-}$ complexes have been prepared where the cation is thought to be interacting with the anion. When the anion is [*H*-1,10-phenanthroline-*N*-oxide]$^+$, it hydrogen bonds to a $[Pd_2Cl_6]^{2-}$ cation [240]. Similarly in $(N_2H_5)_2[PdCl_4]$ the cation coordinates to the palladium [241]. When $[NiL_3]^{2+}$ (L = 1,10 phenanthroline, 4,7-diphenyl-1,10-phenanthroline) is employed as cation the complex shows an irreversible colour change on heating which is caused by migration of the ligand L between metal ions [242]. The reaction of L = diethyl-8-quinolylmethylphosphate with $[PdX_4]^{2-}$ (X = Cl, Br) results in PdL_2X_2 in neutral solution but gives $(HL)_2[PdX_4]$ in acidic conditions [243].

The halide ligand has been used to bridge a variety of metal ions in the reaction of $PdR_2(PhCN)$ with *cis*-MX_2L_2 (M = Ni, Pd, Pt; X = Cl, Br, I, SCN; R = C_6F_5, $C_6H_2F_3$-2,4,6; L = PEt_3, PPh_2Me, C_5H_5N; L_2 = $Ph_2PCH_2CH_2PPh_2$) to give $R_2Pd(\mu\text{-}X)_2ML_2$ [244]. The crystal structure of *cis*-Pd{2,6-dimethyl-C_6H_3NC}$_2Cl_2$ has been determined and shows a linear chain arrangement of palladium atoms [245]. Reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with $(\eta^6\text{-}PhCH_2ZnCl)Cr(CO)_3$ gave the mixed metal complex (18) [246].



(18)

Carbonylation of $[Pd(R)Cl(\mu\text{-}Cl)]_2^-$ (R = 2-methyl-6-nitrobenzene, 2,4,6-trinitrobenzene) gives the monomeric complex $Pd(R)Cl_2(CO)$ which has been crystallographically characterised [247].

4.3 PALLADIUM(I)

A series of $[PdLL']^{2-}$ complexes have been synthesized where L and L' are chelating phosphine ligands with varying bite sizes. The half-wave potential for Pd(II/0) increases with bite size and the palladium(I) complex $[Pd(1,2\text{-}(Ph_2PCH_2)_2C_6H_4)_2]$ was found to be stable [248]. The palladium(I) complex $[PdCl(\mu\text{-}Me_2PCH_2PMe_2)]_2$ reacts with $MeNO_2$ to give C-H activation and palladium oxidation to $[PdCl(CH_2NO_2)(\mu\text{-}Me_2PCH_2PMe_2)]_2$ [249]. The reactivity of the acetylene bridged complex $[Pd_2(\mu\text{-}PhCCPh)(\eta\text{-}Cp)_2]^+$ has been studied with a variety of bipy and phosphorus donor ligands. The acetylene bridge remains unchanged throughout and the Cp ligands are substituted [250].

4.4 PALLADIUM(0)

A patent has appeared on the manufacture of $Pd(PPh_3)_4$ by hydrazine reduction of palladium(II) chloride [251]. Some mixed ligand palladium(0) complexes PdLL' (L = bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,1-bis(diphenylphosphino)-ferrocene; L' = dibenzylideneacetone, 2,3,5,6-tetrachloro-1,4-benzoquinone, 2,3-dichloro-1,4-naphthoquinone) have been synthesized [252].

Protonation of $[Pd\{\mu\text{-}P(CMe_3)_2\}PH(CMe_3)_2]_2$ leads to the protonation of a Pd-(μ-P) bond according to NMR spectroscopic data [253]. Palladium(0) phosphine complexes have also been protonated to give $[PdL_3H]^+$ (L = PPh_3, PPh_2Me, PEt_3) ions whose fluxionality has been studied. $Pd(CO)(PPh_3)_3$ has also [254] been protonated to give $[(Ph_3P)_4Pd_2(\mu\text{-}CO)(\mu\text{-}H)]^{2+}$. Phenol reacts [255] photochemically with $Pd[P(CMe_3)_2]_2$ to give transfer of hydrogen from phenol to phosphine ligand and η^4-coordination of phenoxide to a Pd_2 framework.

Several new palladium carbonyl phosphine clusters have been synthesized including $Pd_{16}(CO)_{13}(PEt_3)_9$ [256] and $Pd_{23}(CO)_{22}(PR_3)_{10}$ (R = Et, n-Bu) [257]. A dimeric complex with pendant ferrocenyl groups, Pd_2L_3 (L = 4-ferrocenyldibenzylideneacetone) has been synthesised [258] and shows a ferrocenyl based oxidation at 0.50 V and a dipalladium based one at 1.21 V. Mixed metal aryl-palladium complexes have been prepared [259] by the reaction of $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ with palladium(0) complexes such as $Pd(PPh_3)_4$ and $Pd(dba)_2$.

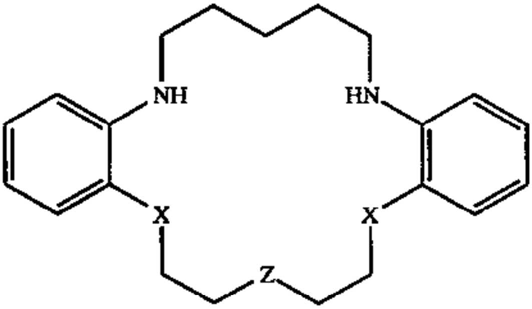
4.5 EXTRACTION

There is a continuing interest in coordinating ligands to palladium(II) so that the complex can be selectively extracted from aqueous media to an organic solvent. The mechanism of solvent exchange in square planar palladium(II) complexes has been investigated by high pressure NMR and found to be associative for a wide range of coordinating solvents [260]. A number of extraction systems have been investigated over the past year (Table 9). The ligand generally has a strong coordinating group such as nitrogen or sulphur atoms and is lipophilic.

Table 9: Extraction systems for palladium(II).

Solvent System	Extractant	Reference
Aqueous perchlorate/xylene	Thiocyanate	[261]
HCl/organic acids	tri-*n*-octylamine	[262]
HCl and base metals	Dibutyl dithiophosphate	[263]
Weak HCl or HBr/chloroform	*o*-xylylene bis(pyrrolidinedithiocarbamate) and *o*-xylylene bis(diethyldithiocarbamate)	[264]
Weak HCl	α-aminophosphonates	[265]
NaCl, HCl, $NaSO_4$, H_2SO_4/*o*-xylene	tri-*n*-octylamine	[266]
Chloride soln with some SCN/toluene	tri-isobutylphosphine sulphide	[267]
	2-hydroxy-5-*t*-nonylbenzaldehyde oxime, 2-hydroxy-5-*t*-octylacetophenone oxime, 2-hydroxy-5-*t*-octylbenzophenone oxime	[268]
HCl/*o*-xylene	trioctylphosphine oxide	[269]
HCl/toluene	*N,N*-dioctylglycine	[270]

A synergistic extraction effect is noticed when a primary [271] or tertiary [272] amine is used in conjunction with 1-phenyl-2-methyl-4-benzoyl-pyrazol-5-one. A couple of macrocyclic extractants have been used; hexameric *p*-*t*-butylcalix[6]arene extracts palladium(II) from alkaline ammonia solution to dichloromethane and other organic solvents [273]. The dibenzo-18-crown-6 analogue (**19**) (X = O, S; Y = $MeC_6H_4SO_2N$, O, S, CH_2; Z = O, S, CH_2) has also been used to extract [274] palladium(II) from aqueous solution over a range of pH.



(19)

The separation of palladium(II) from other platinum group metals has been achieved using centrifugal partition chromatography and trioctylphosphine oxide as ligand [275]. Palladium(II) can be separated from platinum(IV) and copper(II), nickel(II) and cobalt(II) using a tertiary diamine extractant [276]. Iron(III) is also carried through but can be removed by other means.

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