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1. Palladium

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INTRODUCTION

Palladium belongs to the highly potent Group 10 triad (Ni, Pd and Pt) of transition metals. A diverse range of chemistry is displayed by these metals especially by platinum and palladium, and to cover even one year of activity is a challenging task. This review is not a comprehensive survey of palladium chemistry in the year 1990, but, examples are selected to highlight important features. A highly descriptive article on platinum and palladium has recently been published [1] to which the readers are referred for earlier work. The first part of the chemistry presented here is devoted to the coordination complexes of palladium in its +1 to +4 oxidation states. The catalytic aspects of Pd(0) and Pd(II) complexes in various organic transformations are presented in the second part of the review. We would like to thank Professor the Lord Lewis and Dr. Edwin C. Constable (University Chemical Laboratory, Cambridge, U.K.) for their valuable suggestions and Dr. Catherine E. Housecroft (University Chemical Laboratory, Cambridge, U.K.) for editorial corrections. We thank the Cambridge Crystallographic Data Base for access to crystallographic coordinates to enable the redrawing of figures.

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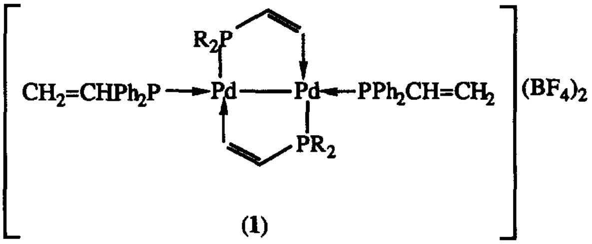
COORDINATION COMPLEXES

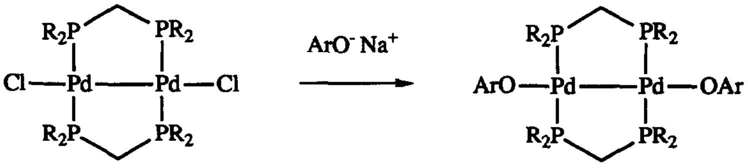
1.1 PALLADIUM (I)

An "unusual" palladium(I) phosphaallyl complex, $[(Ph_2PCH{=}CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH{=}CH_2)Pd(I)]_2(BF_4)_2$ (1) has been prepared [2] from the photochemical reaction of $(Ph_2PCH{=}CH_2)_2PdCl_2$ with a slight excess of $AgBF_4$. The neutral vinylphosphine acts as a bridging $\mu\text{-}\eta^3$-four electron donor to the palladium(I) centres.



(1)

Metathetical exchange of Cl^- ions with OAr^- in the reactions of $Pd_2L_2Cl_2$ (L = *bis*(dimethylphosphino)methane or *bis*(diphenylphosphino)methane) (2) with excess sodium or potassium aryloxides yields the dinuclear palladium (I)–OAr complexes (3) [3]. The crystal structure of the trifluoroacetate complex, $Pd_2(dppm)_2(OCOCF_3)_2$ (4) shows a *cis*-orientation of the carboxylates and a twist-boat configuration of the palladium-phosphorus-carbon ring system.



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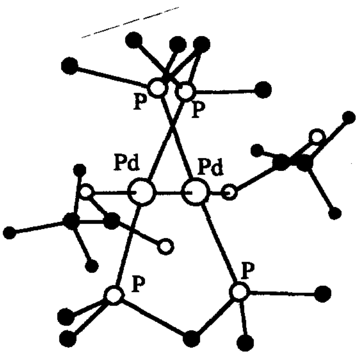


Axial groups = $CF_3C(O)O\text{-}$

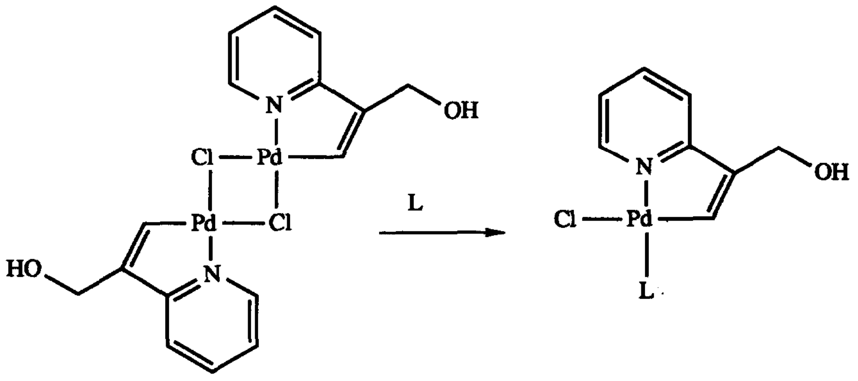
For the phenyl substituents, *ipso* C atoms only are shown

(4)

1.2 PALLADIUM (II)

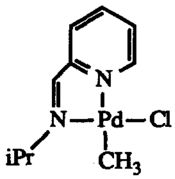
1.2.1 Complexes with nitrogen based donor ligands

It has been shown that 2-vinylpyridine forms the dimeric cyclometallated complex, [*bis*(μ-chloro)*bis*[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*)]dipalladium(II)] (**5**) which reacts with donor ligands, L, such as pyridine or PPh_3 to give monomeric complexes (**6**) [4]. The monomeric complex with L = PPh_3 has been structurally characterised.

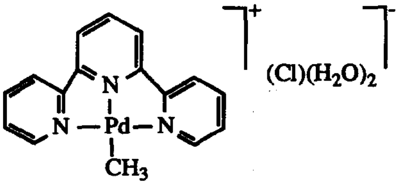


(**5**) (**6**)

Nitrogen based tridentate ligands have been used to prepare palladium(II) complexes (**7**) and (**8**) starting from $Pd(cod)Cl_2$ by ligand displacement [5]. Neutral or cationic species are obtained depending on the nature of the coordinating ligand. These complexes have been structurally characterised.

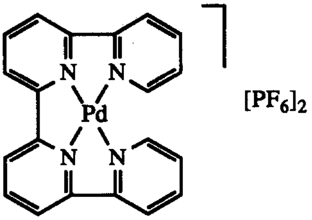


(**7**)



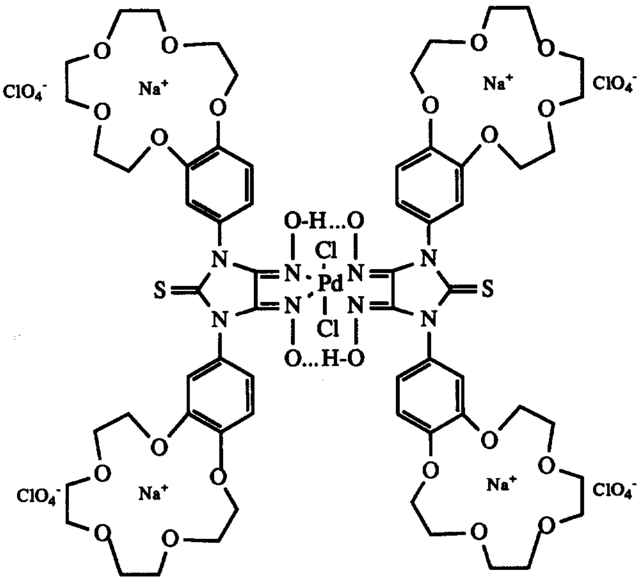
(**8**)

Palladium (II) complexes of oligopyridine ligands 2,2':6'2":6"2'''-quaterpyridine (quaterpy), $[Pd(quaterpy)][PF_6]_2$ and 2,2':6'2":6"2''':6'''2''''-quinquepyridine (quinquepy), $[Pd_2(quinquepy)_2][PF_6]_4.4MeCN$ have been reported [6]. A distorted square planar geometry of the quaterpy ligand around the palladium atom was confirmed by an single-crystal X-ray diffraction study of $[Pd(quaterpy)][PF_6]_2$ (**9**). The complex, $[Pd_2(quinquepy)_2][PF_6]_4$ exhibits a double helical structure.



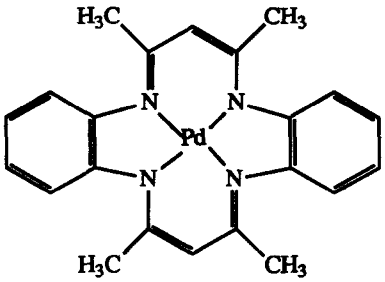
(**9**)

A *vicinal* dioxime ligand, 1,3-*bis*(benzo-15-crown-5)-2-thioxo-4,5-*bis*(hydroxyimino)-imidazoline has been used to prepare the palladium(II) complex (**10**) with a metal to ligand ratio of 1:2; coordination is through *N*-donors [7].



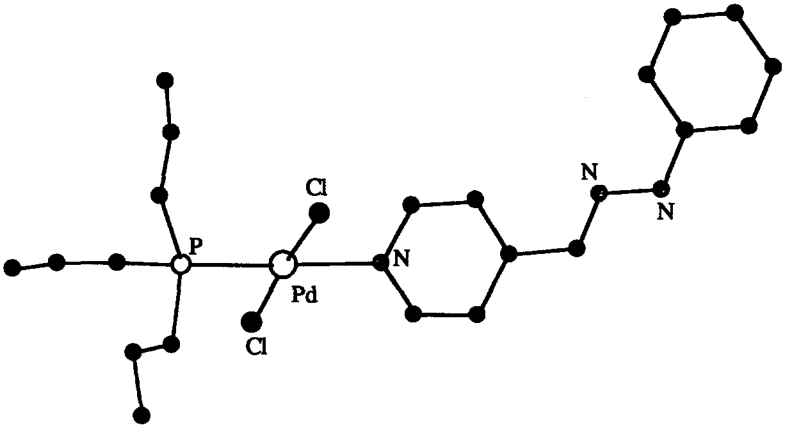
(**10**)

A palladium(II) complex of 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine (**11**) has been reported [8].



(11)

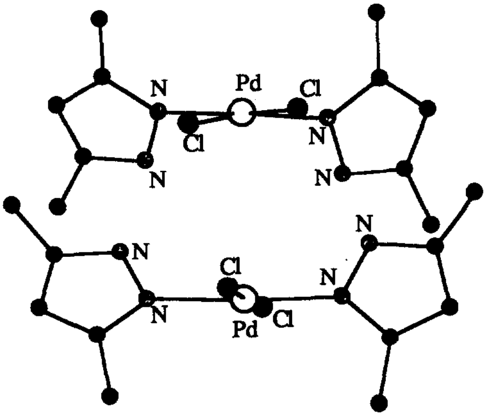
Dichloro(4-pyridinecarbaldehydephenylhydrazone)(tri-*n*-propylphosphine) palladium(II) (**12**) has been prepared from the reaction of $[Pd_2(PPr^n_3)_2Cl_4]$ and 4-pyridinecarbaldehyde phenylhydrazone. The X-ray crystal structure of the complex shows a square planar palladium atom with the hydrazone ligand coordinated through the pyridine *N*-atom in a *syn* configuration and the two chlorides in *trans* positions [9].



(12)

A palladium(II) complex of 3,5-dimethylpyrazole, $[Pd\{3,5\text{-}(CH_3)_2C_3H_2N_2\}_2Cl_2]$, (**13**) has been synthesised and structurally characterised. The crystal structure shows a square planar environment around the palladium atom with the chloride ligands in a *trans* configuration. The pyrazole ligand coordinates to palladium through only one nitrogen atom and the other nitrogen atom is attached to the chloride via a hydrogen bonding interaction [10].

Palladium(II) complexes of *b*-carboline alkaloids, 3*H*, 9*H*-pyrido-[3,4-*b*]indole (Harmaline, Harmane) (**14, 15**) have been reported [11].



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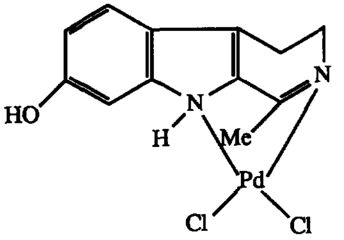

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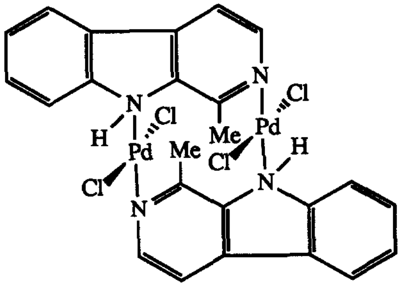
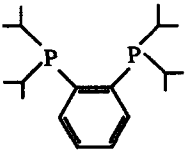


(15)

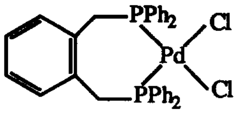
1.2.2 Complexes with phosphorus based donor ligands

Reaction of $(PhCN)_2PdCl_2$ with the chelating phosphine, o-phenylene*bis*-(diisopropylphosphine) **(16)** (abbreviated as DH by the authors for its suggested resemblance to a deer's head) yields *cis*-(DH)$PdCl_2$ [12].



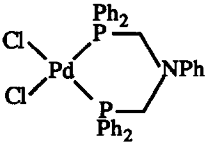
(16)

The chelating ligand, 1,2-*bis*[(diphenylphosphino)methyl]benzene, which has the ability to form a seven membered ring upon coordination to a metal, has been used to synthesize the stable square planar palladium(II) complex, *cis*-$Pd(L)Cl_2$ (17) [13].



(17)

The preparation of palladium(II) complexes of *bis*(diphenylphosphino)methanide $[Pd(C_6F_5)(Ph_2PCHPPh_2)(PR_3)]$ have been reported. Synthesis of such complexes involves the reaction of Pd-halo complex $PdCl(C_6F_5)(PR_3)_2$ with *bis*(diphenylphosphino)methane in the presence of NaH, or prior deprotonation of the chelating phosphine with BuLi and then reaction with the Pd-halo complex [14]. Polydentate mixed phosphine/amine ligands $Ph_2PCH_2NPh_2$, $Ph_2PCH_2N(Ph)CH_2PPh_2$, $Ph_2NCH_2PPhNPh_2$ and $(Ph_2PCH_2)_2N(CH_2)_2N(CH_2PPh_2)_2$ are coordinated to palladium to give complexes of the type shown in (18) and (19) [15].



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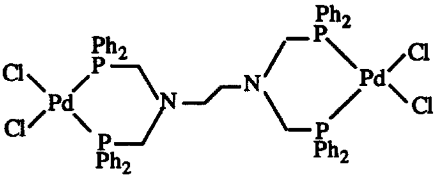
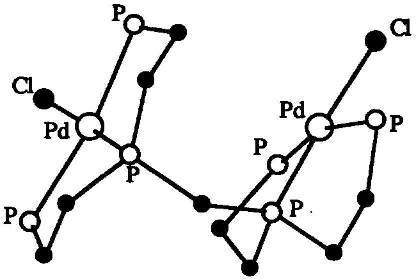


(19)

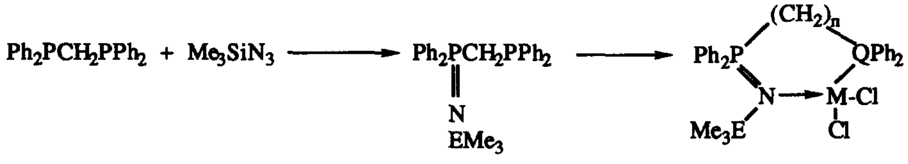
A bimetallic complex containing the hexadentate *P*-donor ligand $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$ (eHTP) coordinated to palladium in both chelating and bridging positions $[Pd_2Cl_2(eHTP)][PF_6]_2$ (20) has been prepared and structurally characterised [16]. Each palladium centre is shown to have a distorted square planar geometry with a partially closed geometry being adopted by the phosphine ligand.



(20)

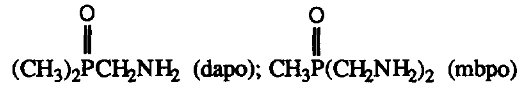
1.2.3 Complexes with mixed donor ligands

The heterobifunctional coordinating ligands phosphoranimine phosphines and arsines have been used to prepare palladium(II) metallacycles, [RN=PPh$_2$(CH$_2$)$_n$EPh$_2$PdCl$_2$] (R = SiMe$_3$, GeMe$_3$, H; n = 1, 2; E = P, As) (**21**); the complex [NH=PPh$_2$CH$_2$PPh$_2$PdCl$_2$] has been structurally characterised [17].



(21)

cis-Square planar palladium(II) complexes of amino substituted phosphine oxides, [Pd(dapo)Cl$_2$] and [Pd(mbpo)Cl$_2$] (dapo = dimethylamino methylphosphine oxide and mbpo = methyl *bis*(aminomethyl)phosphite oxide (**22**)) have been reported [18]. A platinum analogue of such complexes, [Pt(NH$_3$)(dapo)Cl$_2$] shows high antitumour activity.

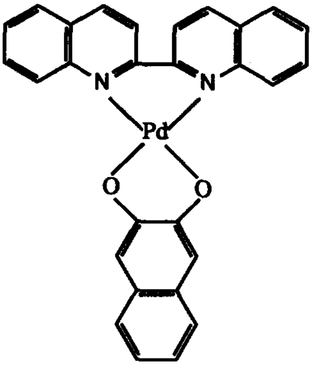


$(CH_3)_2\overset{\overset{O}{\|}}{P}CH_2NH_2$ (dapo); $CH_3\overset{\overset{O}{\|}}{P}(CH_2NH_2)_2$ (mbpo)

(22)

Mixed ligand complexes containing nitrogen donors (*N-N*) such as 2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 2,2'-biquinoline and oxygen donors (*X-X*) such as dianions of catechol, 4-^{t}butylcatechol or 2,3-dihydroxynaphthaline, [Pd(N-N)(*X-X*)] (**23**) have been prepared by the reaction of [Pd(*N-N*)Cl$_2$] with oxygen donor ligands in dmso containing a small amount of 1M NaOH [19].

The macrocyclic *vic*-dioxime ligand with two crown ether groups, 1,2-*bis*-[(monoaza[15]crown-5-*N*-yl]-glyoxime (**24**) coordinates to palladium(II) and the resulting complex has been structurally characterised (**25**) [20].



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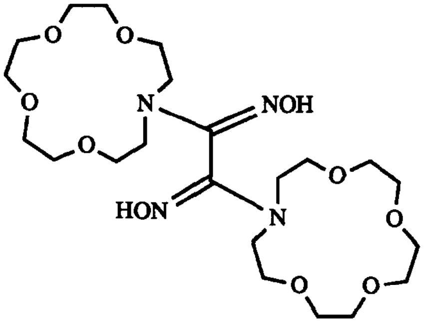

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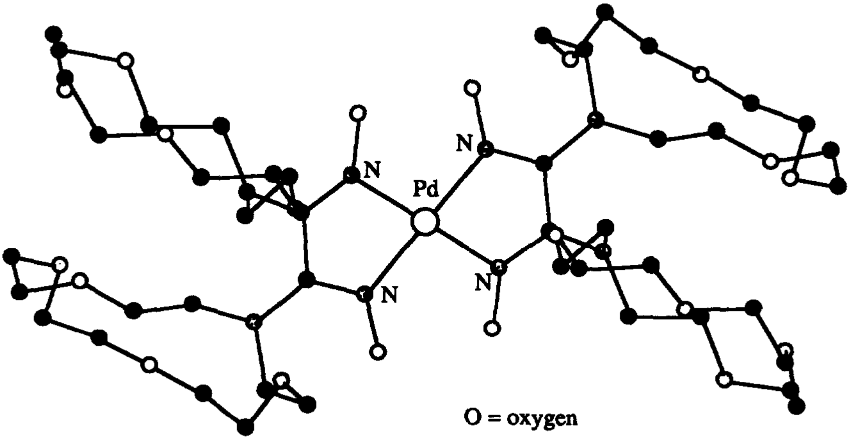
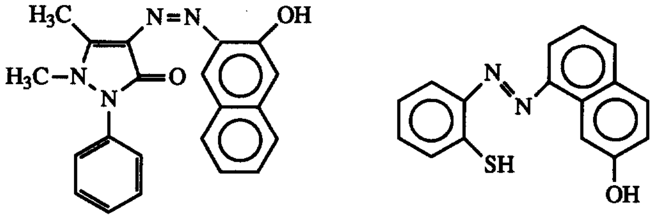
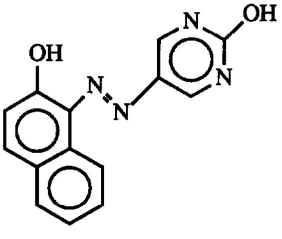


(25)

Palladium(II) complexes of type $PdCl_2L_2$ containing mixed-donor sets of oxygen-nitrogen atoms and nitrogen-sulfur atoms where L = 5-aminouracil, 4-aminoantipyrine, 4-nitroantipyrine, 2-aminobenzenethiol, antipyrineazonaphthol, benzenethiolazonaphthol and uracilazonaphthol **(26)** have been prepared from $PdCl_2$ and the desired ligand in an acidic methanol solution [21].

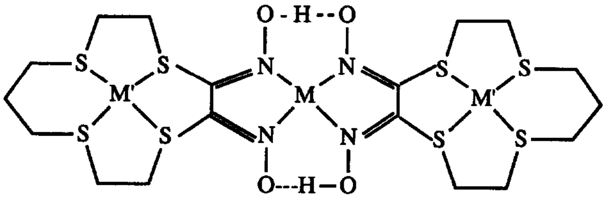


Antipyrineazonaphthol **(26)** Benzenethiolazonaphthol



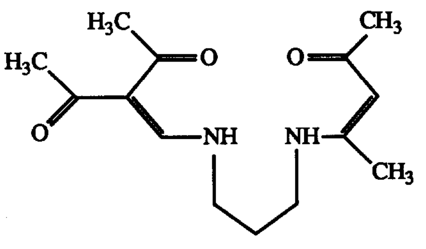
Uracilazonaphthol

The palladium(II) complex **(27)** containing the quadridentate tetrathiamacrocycle, 2,3-*bis*(hydroxyimino)-1,4,7,11-tetrathiacyclotridecane, with a metal to ligand ratio of 3:2 has been reported. Mixed metal complexes of this ligand with M = Pd(II), M' = Ni (II) or Cu (II) have also been prepared. These complexes are paramagnetic [22].

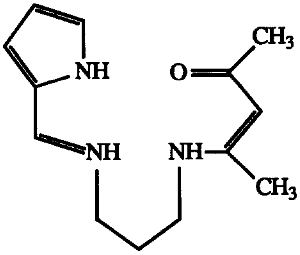


(27)

Palladium(II) complexes containing unsymmetrical Schiff-base ligands (**28, 29**) in which there is coordination of oxygen and nitrogen atoms to a square planar palladium centre have been prepared [23].

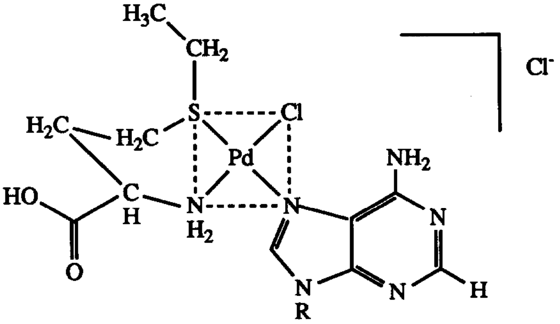


(**28**)



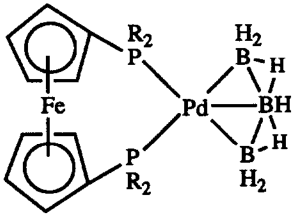
(**29**)

Mixed ligand complexes containing the amino and nucleic acids guanosine, inosine and cytosine with *cis*-dichloroethioninepalladium(II), chloroethionine(L)palladium(II)chloride (**30**) have been reported [24].



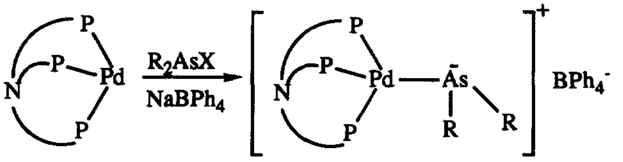
(**30**)

An interesting palladium(II) complex 1-[1,1'-*bis*(diphenylphosphino)ferrocene]palladatetraborane, (**31**) (R = Ph) containing two phosphorus donors attached to the ferrocene moiety and the triborane ligand $[B_3H_7]^{2-}$ has been prepared and structurally characterised [25].



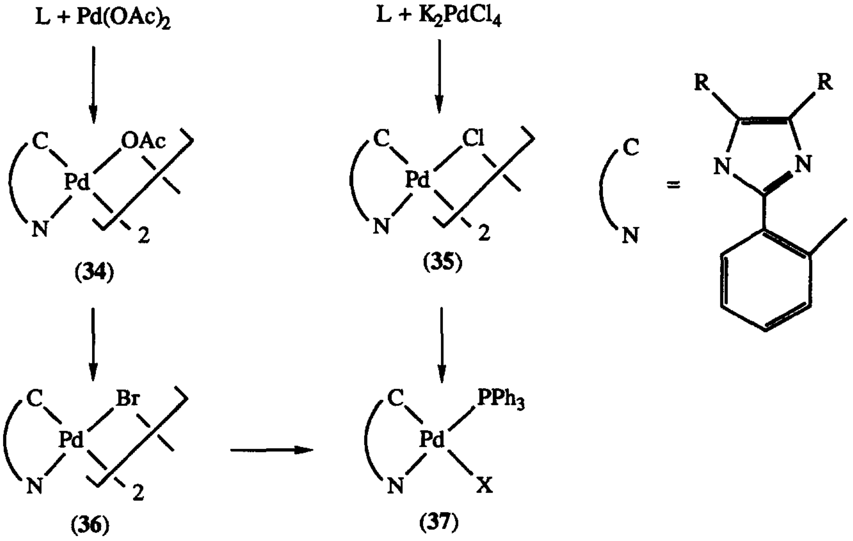
(**31**)

Complexes containing terminal arsenido groups $[(N(CH_2CH_2PPh_2)_3)PdAsR_2]BPh_4$ (33) (R = Me, Ph) have been prepared from Pd(0) complexes $[(N(CH_2CH_2PPh_2)_3)Pd]$ (32) by the oxidative addition of R_2AsX (X = I, Cl). A corresponding platinum analogue, $[(NCH_2CH_2PPh_2)_3)Pt(AsPh_2)][BPh_4]$ has been structurally characterised [26].



(32) (33)

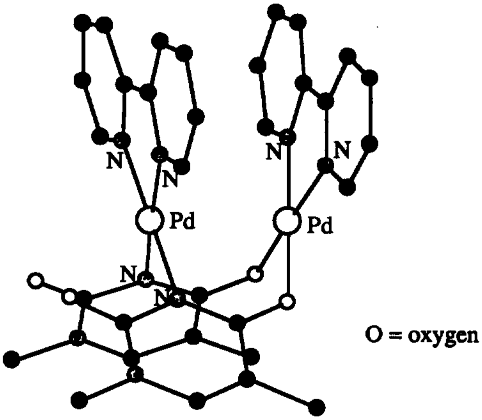
Cyclometallated acetato or chloro bridged dimeric Pd(II) complexes of 1-methyl-phenylimidazoles (34), (35) or (36) have been synthesised by the reaction of palladium(II) acetate or potassium-tetrachloropalladate(II) with the corresponding imidazole. The dimeric complexes react with nucleophiles such as PPh_3 to give monomeric complexes of type $LPd(X)PPh_3$, (37) [27].



(34) (35) (36) (37)

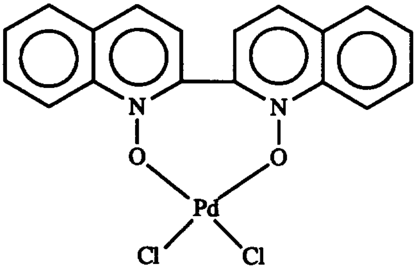
Uracil and thymine nucleobase anions have been used to prepare nitrogen-bound monomeric and nitrogen-bound, oxygen-bridged dimeric palladium(II) complexes. The complex, [(bpy)Pd(1-

methylthymine)$_2$Pd(bpy)][NO$_3$]$_2$.5.5H$_2$O (38) has been structurally characterised in which the two thymine ligands are arranged head-to-head around two square planar Pd centres [28].



(38)

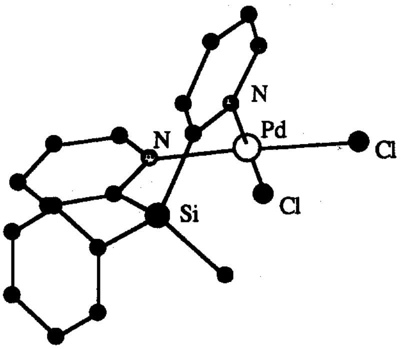
A fluorescent Pd(II) complex (39) with the ligand 2,2"-biquinolyl-*N,N'*-dioxide has been reported [29].



(39)

Palladium(II) complexes of *bis*(2-pyridyl)silane ligands, [R'R"Si(2-pyridyl)]PdCl$_2$, have been prepared and the square planar complex (CH$_3$)(C$_6$H$_5$)Si(2-pyridyl)PdCl$_2$ (40) has been structurally characterised. The six-membered chelating ring of the silicon-containing ligand is in a boat conformation [30]. The complex [Me$_2$Si(2-pyridyl)]PdCl$_2$ has been shown to catalyse the cross coupling of vinyltributylstannane with benzoyl chloride.

Bis(dialkylphosphonate)palladium(II) complexes, [(R'$_3$P)ClPd{P(O)(OR)$_2$}$_2$H] (R = Me, Et; R' = Et, Ph) (41, 42) containing secondary alkylphosphite and alkylphosphonate as chelating ligands have been reported [31].



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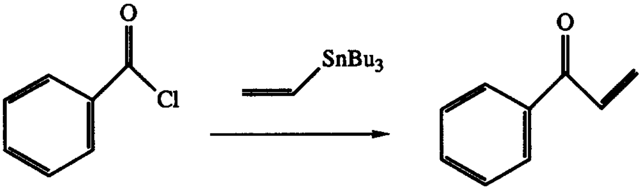

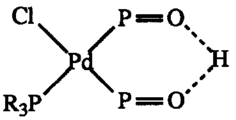

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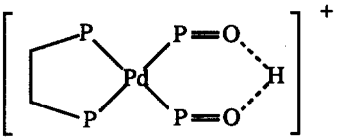
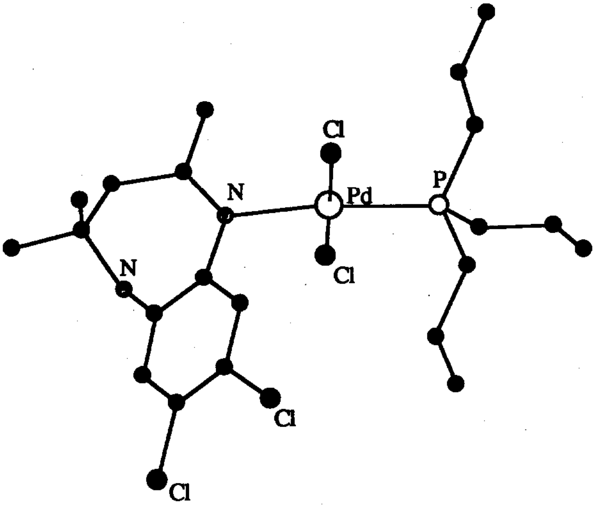


(42)

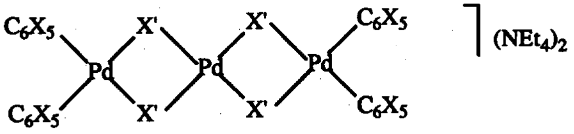
The reaction of [$Pd_2Cl_4(PPr^n{}_3)_2$] with 7,8-dichloro-2,3-dihydro-2,2,4-trimethyl-1*H*-1,5-benzodiazepine yields a square planar palladium(II) complex (43) in which the 1,5-benzodiazepine ligand is bound to the metal through its nitrogen atom as confirmed by X-ray single-crystal analysis [32].

Tri- and tetranuclear palladium(II) complexes, $[NEt_4]_2[(C_6X_5)_2Pd(\mu\text{-}X')_2Pd(\mu\text{-}X')_2Pd(C_6X_5)_2]$ (44), $[NBu_4]_2[(C_6X_5)_2Pd(\mu\text{-}X')_2Pd(\mu\text{-}X')_2Pd(\mu\text{-}X')_2Pd(C_6X_5)_2]$ (X = F, Cl) (45) containing Pd centres doubly bridged by halide anions have been isolated from the reactions of $[PdX_4]NEt_4$ or $[Pd_2X'_6]NBu_4$ with *cis*-$[Pd(C_6X_5)_2(THF_3)_2$ [33].

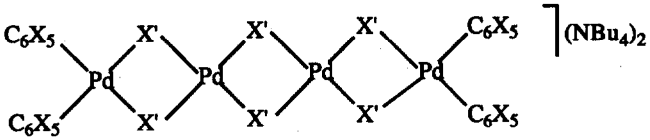
The complex disodium *bis*(N-tosylglycinato-*N*,*O*)palladate(II) containing the *N*-tosyl derivative of glycine, has been prepared. An X-ray crystal structural determination of this complex (46) shows a square planar metal atom with the two *N*-tosyl ligands bound through their amide-nitrogen and carboxylate-oxygen atoms in a bidentate fashion [34].


Cl
N
Pd
P
N
Cl
Cl
Cl

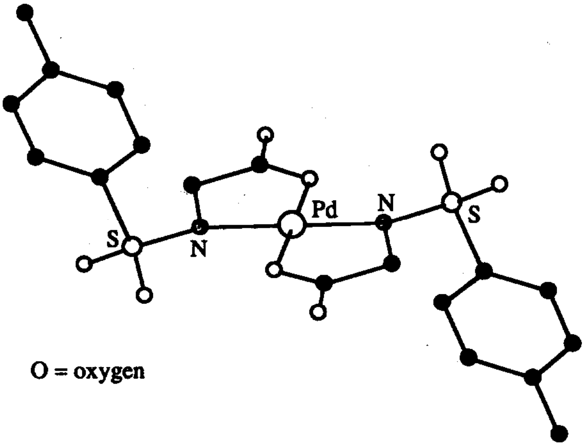
(43)


C6X5
X'
X'
C6X5
Pd
Pd
Pd
C6X5
X'
X'
C6X5
(NEt4)2

(44)

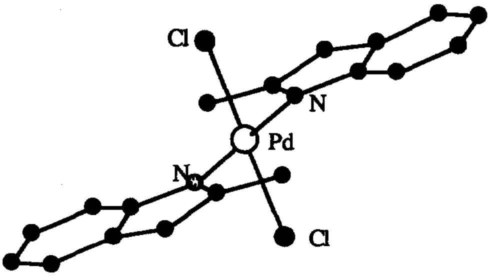

C6X5
X'
X'
X'
C6X5
Pd
Pd
Pd
Pd
C6X5
X'
X'
X'
C6X5
(NBu4)2

(45)


Pd
N
S
S
N
O = oxygen

(46)

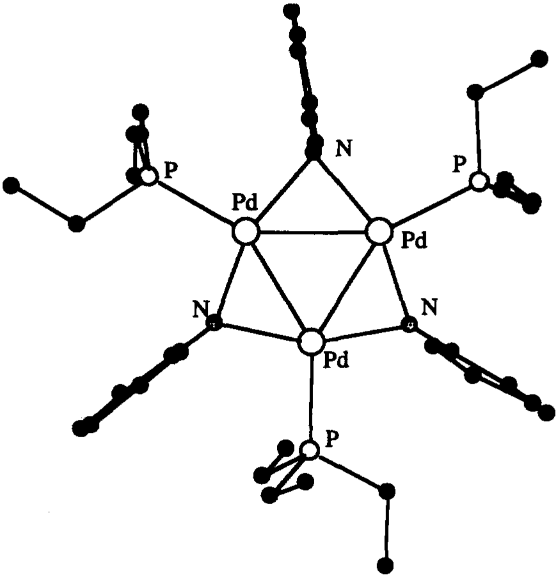
trans-[Pd(alkyl-indole)$_2$Cl$_2$] (alkylindole = 2-methylindole or 2,5-dimethylindole) complexes in which the indole ring is coordinated to the metal atom through the nitrogen atom in 3-H form have been prepared from [PdCl$_4$]$^{2-}$ (the sodium salt) and the corresponding indole in methanol. An X-ray crystal structural investigation of these complexes indicates a square planar Pd(II) environment (47) with the indole rings in a *trans*-configuration around the metal [35].



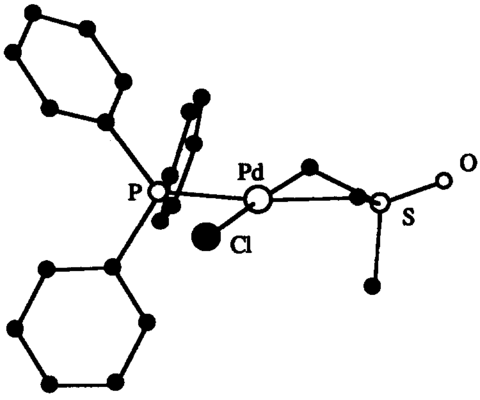
(47)

Single-bridged polynuclear *pseudo*-halo complexes of palladium(II), e.g., *cis*-(C$_6$F$_5$)$_2$Pd[(-NC or SCN)-*trans*-Pd(C$_6$F$_5$)(PPh$_3$)$_2$]$_2$ have been prepared by the reaction of Pd(C$_6$F$_5$)$_2$(THF)$_2$ with *trans*-Pd(CN)$_2$(C$_6$F$_5$)(PPh$_3$)$_2$ in a 1:2 ratio [36].

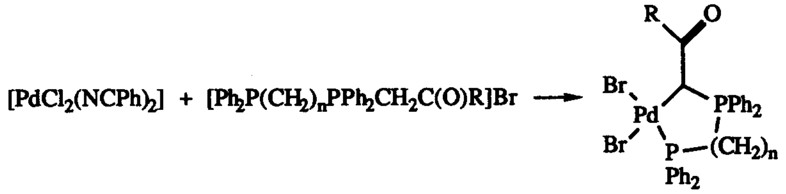
A Pd(II) trinuclear complex containing bridging amido and imido ligands, [Pd(PEt$_3$)$_3$(μ_2-NPh)$_2$(μ_2-NHPh)]Cl has been prepared by the reaction of the anion [PhNN=NNHCH$_2$CH$_2$NH]$^{2-}$ (Li(THF) salt) with *cis*-PdCl$_2$(PEt$_3$)$_2$. This triangular Pd$_3$ cluster, (48), has been structurally characterised; it has D_{3h} symmetry and 42 valence electrons [37].



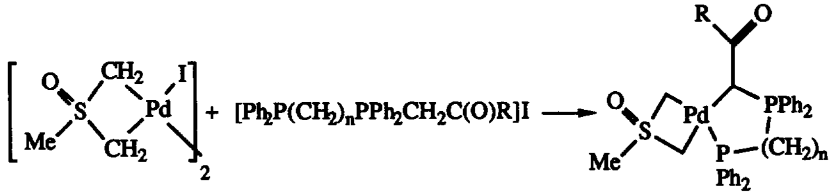
(48)



(49)



(50)

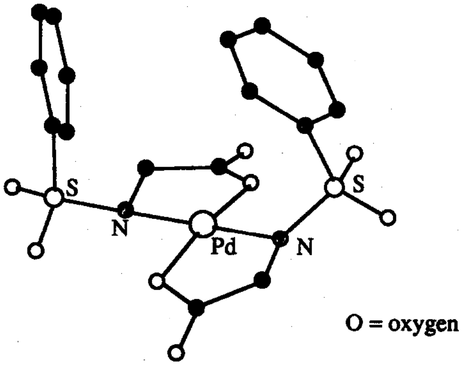


(51)

The two sulfur ylide complexes $\{Pd(PPh_3)_2[(CH_2)_2S(O)(CH_3)_2]\}I$ and $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ have been prepared by a phase transfer reaction of $Pd(PPh_3)_2Cl_2$ with trimethylsulfoxonium iodide in NaOH. The crystal structure of the complex $Pd(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ **(49)** shows the palladium atom to be in a square planar environment with short S-C bond lengths associated with the ylide and small C-Pd-C angles [38]. Phase transfer catalysis has also been employed for the synthesis of the palladium-phosphorus-ylide, $[PdBr_2\{Ph_2P(CH_2)_nPPh_2CH(CO)R\}]$ ($n = 1$ or 2; R = Me, Ph or OEt) **(50)** and the palladium sulfur-phosphorus ylide complexes, $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2P(CH_2)_nPPh_2$-

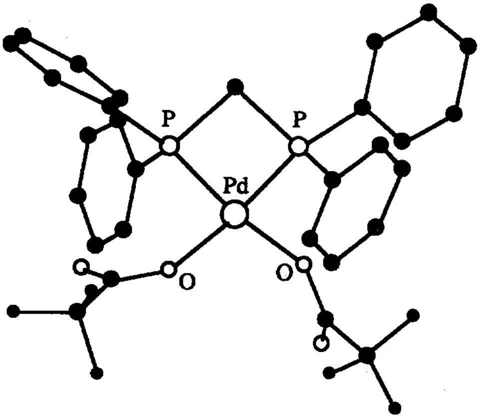
CHC(O)R}]I (51). The X-ray crystal structure of the mixed-ylide complex $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2PCH_2PPh_2CHC(O)Ph\}I.CH_2Cl_2.H_2O$ shows that the Pd-C bond (2.183(5) Å) involved in the coordination of the phosphorus-ylide is longer than that involved in the coordination of the sulfur-ylide (2.094(3) Å) [39].

Disodium *bis*(*N*-benzenesulfonylglycinato-*N*,*O*)palladate(II) monohydrate, (52), has been synthesised and structurally characterised. The bidentate *N*-benzenesulfonylglycine dianion is coordinated to the palladium atom through the carboxylate oxygen and the sulfonamide nitrogen atoms giving a slightly distorted square planar geometry about the metal centre [40].



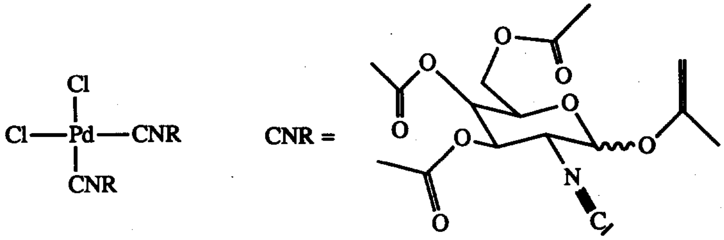
(52)

The synthesis and structural characterisation of *bis*(diphenylphosphino)methane]-*bis*(trifluoroacetato)palladium(II) (53) have been reported. The palladium atom is in a *pseudo* square planar environment with very short Pd-P bond distances (2.219(3) and 2.333(3) Å) and a very small O-Pd-O angle of 84.4(4)°. The former strutural feature is attributed to the weak *trans* influence of the trifluoroacetate ligand and the latter to strong electronic influence of the phosphine [41].



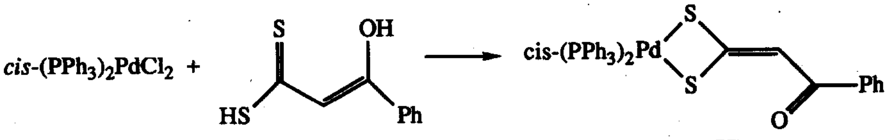
(53)

A Pd(II) complex of 1,3,4,6-tetra-O-acetyl-1,2-deoxy-2-isocyano-$\alpha(\beta)$-D-glucose, abbreviated to CNR, (54), *cis*-$Cl_2Pd(CNR)_2$ has been reported [42].



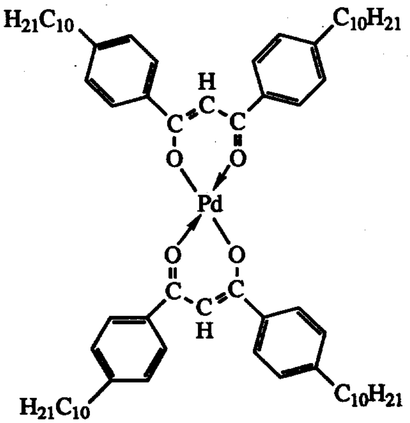
(54)

A 2-benzyl-1,1-ethenedithiolate Pd(II) complex, $(PPh_3)_2Pd[S_2C{=}CHC(O)C_6H_5]$ (55) has been prepared by the reaction of β-hydroxydithiocinnamic acid with $(PPh_3)_2PdCl_2$ [43].



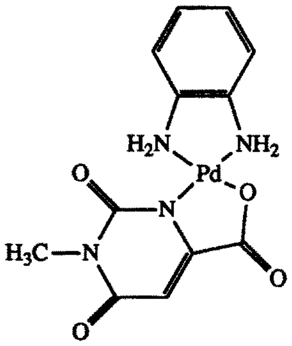
(55)

The synthesis and crystal structure of *bis*[1,3-di(4-^{n}decyl-phenyl)propane-1,3-dionato]palladium(II) (56), have been reported; the complex exhibits discotic mesomorphism [44]. The palladium centre is in a square planar environment created by the four oxygen atoms of the ligand.



(56)

Palladium(II) coordination complexes of 3-methyl-oratic acid, L, $[Pd(R_2)L].nH_2O$ **(57)** (R_2 = $(NH_3)_2$, 1,2-diaminocyclohexane) possessing potential antitumour acitivities similar to their platinum analogues have been prepared [45].

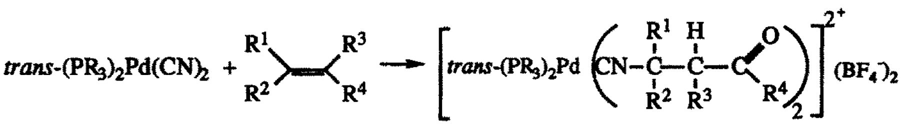


(57)

Monomeric palladium(II) complexes of 1,2-*bis*(diphenylphosphino)ethane (dppe), Pd(dppe)L' (L' = oxalic acid, malonic acid, methylmalonic acid, 1,1-cyclopropanedicarboxylic acid or 1,1-cyclobutanedicarboxylic acid) have been reported [46].

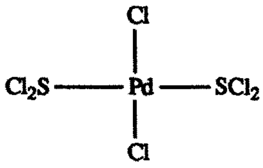
Photosensitisation of 2,2,6,6-tetramethyl-4-piperidinol by the mixed ligand (α-diimine and azide) complexes of palladium, $[Pd(N\text{-}N)(N_3)_2]$ in which *N-N* = 2,2'-bipyridine, 1,10-phenanthroline, 2,2'-biquinoline or 4,7-diphenyl-1,10-phenanthroline has been studied [47]. The photosensitisation ability of these complexes is dependent on the nature of the α-diimine (bipy > phen > biq).

The palladium(II) complexes *trans*-$[(R_3P)_2PdCN\text{-}CR^1R^2\text{-}CHR^3\text{-}C(O)R^4)_2][BF_4]_2$, **(58)**, containing γ-oxoisocyanide as a ligand have been prepared by the reaction of *trans*-$(R_3P)Pd(CN)_2$ with α,β-unsaturated ketones in the presence of $Et_2O\text{-}HBF_4$ [48].



(58)

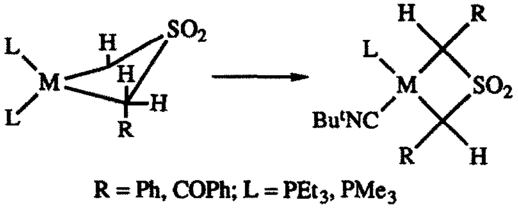
The synthesis and crystal structure of *trans-bis*(dichlorosulfane)palladium(II) chloride, $PdCl_2(SCl_2)_2$, have been reported. $PdCl_2(SCl_2)_2$, **(59)**, is prepared by the reaction of palladium with an excess of sulfur and chlorine. Results of a crystal structure determination show two sulfur dichloride ligands in a *trans*-configuration. The complex decomposes upon heating to give $PdCl_2$ and SCl_2 [49].



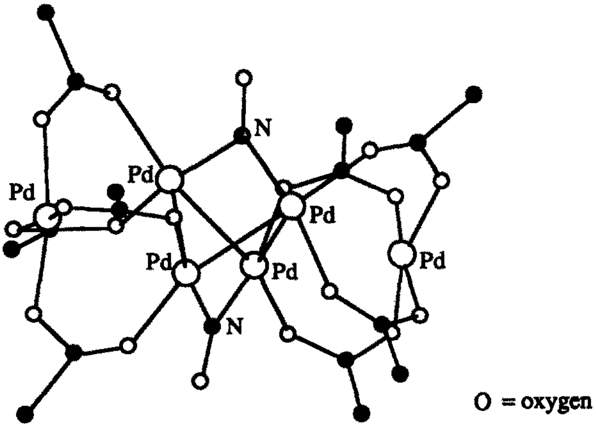
$Cl_2S-PdCl_2-SCl_2$

(59)

Monosubstituted metallathietane-3,3-dioxide complexes of palladium (**61**) have been prepared by a ligand substitution reaction using an excess of alkyl isocyanide with palladium metallacycle (**60**) [50].



(60) (61)

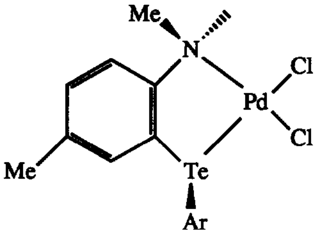


(62)

A palladium (II) dimeric η^3-methylallyltrichlorotin complex, $[Pd(\eta^3\text{-}C_4H_7)(\textit{cyclo}\text{-}1,5\text{-}diene)]_2[Pd(\eta^3\text{-}C_4H_7)(SnCl_3)_3]$ has been characterised by NMR spectroscopy. The corresponding platinum analogue was structurally characterised and found to contain two discrete cationic and anionic Pt(II) centres [51].

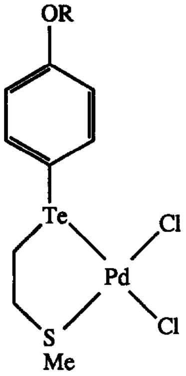
A mixed ligand palladium μ_2-nitrosyl cluster $[Pd_6(O_2CMe)_8(\mu_2\text{-}NO)_2]$, **(62)**, has been prepared and structurally characterised from a reaction involving reduction of nitric acid by CO in an acetic acid solution of $[Pd_3(O_2CMe)_6]$ [52].

Complexes of type **(63)** containing telluride ligands (telluroamines) have been prepared by reacting Na_2PdCl_4 with the corresponding ligand [53]. Monomeric, diamagnetic *cis*-Pd(II) complexes **(64)** of the bidentate ligand 2-(aryltelluro)ethylmethylsulfide have also been prepared [54].



Ar = C_6H_5, 4-$MeOC_6H_4$, 4-EtO-C_6H_4.

(63)



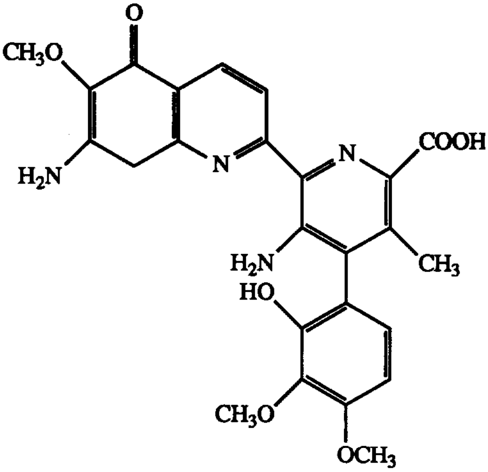
(64)

The η^1-benzyl complex of palladium, chloro(benzyl)*bis*(tricyclohexylphosphine) palladium(II), **(65)**, reacts with potassium tetrachloropalladate(II) to give the η^3-benzyl monophosphine complex, chlorobenzyl(tricyclcohexyl(phosphine)palladium(II), **(66)**, [55].

$$\text{trans-}PdCl_2(PR_3)_2 \longrightarrow \underset{\textbf{(65)}}{[Pd(\eta^1\text{-}CH_2C_6H_5)Cl(PR_3)_2]} \longrightarrow \underset{\textbf{(66)}}{[Pd(\eta^3\text{-}CH_2C_6H_5)Cl(PR_3)_2]}$$

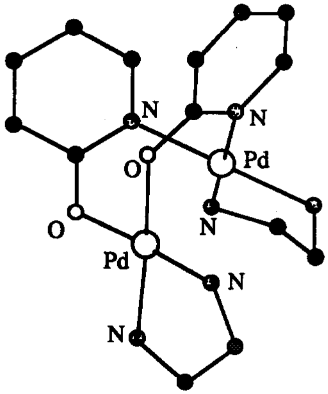
The synthesis and reactivity of $[Pd(H_2O)_2(Ph_2PCH_2CH_2PPh_2)](CF_3SO_3)_2]$ as an acetalisation catalyst have been reported [56]. The complex is prepared by the metathetical reaction of $[PdCl_2(Ph_2PCH_2CH_2PPh_2)]$ with silver trifluoromethane sulfonate in the presence of H_2O.

A 1:1 Pd(II) complex of streptonigrin (**67**), a potential antitumor agent has been isolated from the reaction of $K_2[PdCl_4]$ with the ligand in aqueous media [57].



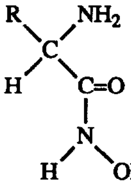
Streptonigrin
(**67**)

A head-to-head binuclear palladium(II) complex, $[Pd_2(en)_2(C_5H_4NO)_2][NO_3]_2$, (**68**), containing α-pyridonate as a bridging ligand has been prepared and structurally characterised. The complex isomerizes to the head-to-tail arrangement in solution [58].



(**68**)

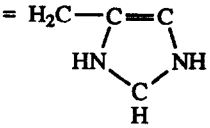
The synthesis of Pd(II) complexes of hydroxamic acids (amino hydroxamic acid (**69**), acetohydroxamic acid (**70**)) and their interaction with glycylglycine (**71**) have been reported [59].



Aminohydroxamic acid

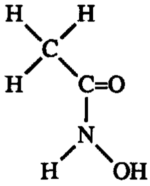
(69)

R = H, Glycine; = CH_2OH, Serine.



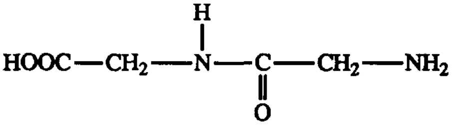
Histidine

= CH_2H_2-S-CH_3, Methionine



Acetohydroxamic acid

(70)

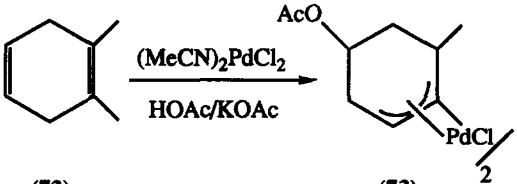


$$HOOC-CH_2-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-CH_2-NH_2$$

Glycylglycine

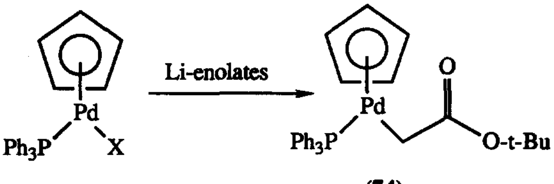
(71)

Addition of an acetate to a variety of alkyl-substituted 1,4-cyclohexadienes **(72)** in an acetic acid solution of *bis*(acetonitrile)palladium dichloride yields *trans-bis*(5-acetoxy-1,2,3-η3-cyclohexenyl)palladium(II) complexes **(73)** by "distil" addition [60].



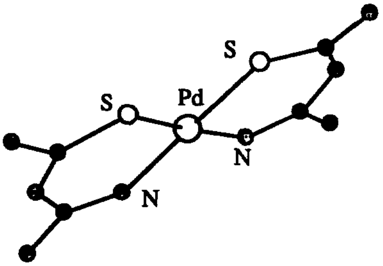
(72) (73)

The synthesis and chemistry of carbon-bound palladium(II) enolates, η^5-$C_5R_5(Ph_3P)PdCHR'COR''$ (R = H, CH_3; R' = H, CH_3; R" = ${}^tBu$, Ph, O-${}^tBu$) **(74)** have been reported [61].



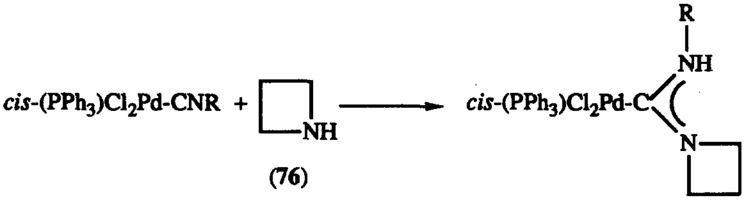
(74)

The synthesis and crystal structure of *bis*(amidinothiourea)palladium chloride have been reported [62]. The two ligands (1-amidino-2-thiourea) are coordinated to *cis*-planar palladium (75) through their sulfur and nitrogen atoms. The $[Pd(SC_2N_4H_6)_2]^{2+}$, Cl^- units and the water molecules are held together by hydrogen bonds.



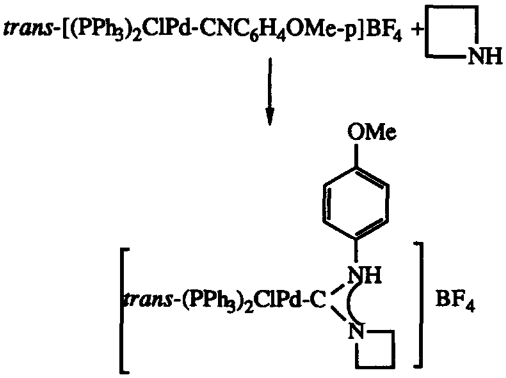
(75)

A detailed investigation of the electronic spectra of the square planar palladium(II) complex, Pd(*bis*(*O,O'*-diethyldithiophosphate) together with the corresponding Ni(II) and Pt(II) analogues has been carried out using pseudopotential valence-only *ab initio* methods and He(I) and He(II) photoelectron spectroscopy [63].



(76)

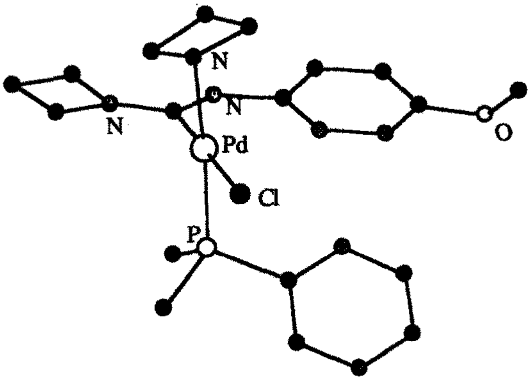
(77)



(78)

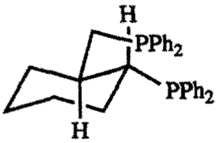
Acyclic diaminocarbene derivatives of azetidine (76) with Pd(II) isocyanide complexes (77, 78) are prepared by reacting *cis*-[$PdCl_2(PPh_3)(CNR)$] (R = C_6H_4OMe-p or Bu^t) or *trans*-[$PdCl(PPh_3)_2(CNC_6H_4OMe$-p)]$BF_4$ with azetidine [64].

The reaction of *cis*-[$PdCl_2(PMe_2Ph)(CN$-C_6H_4-OMe-4)] with two equivalents of azetidine gives the cationic acyclic diaminocarbene complex (79) which has been structurally characterised. It displays a distorted square planar palladium with the diaminocarbene ligand *trans* to the chloride ligand.

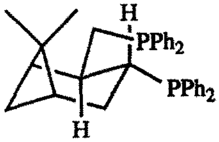


(79)

C_s-symmetrical π-allyl ligands of 1-acetoxy-2-propene, 1-acetoxy-1,3-diphenyl-2-propene and 1-acetoxy-2-cyclohexene have been coordinated to chiral diphosphine (**80**, **81**) palladium units yielding complexes in high stereoselectivities [65].



(80)

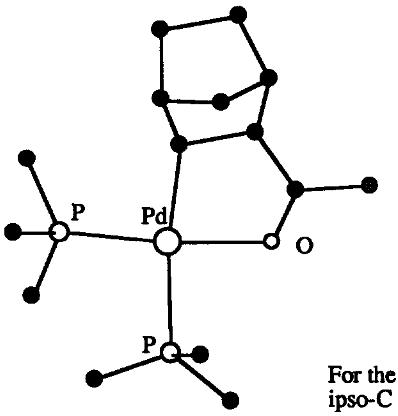


(81)

Insertion of norbornylene into Pd(II)-acyl bond of [$Pd(PPh_3)_2(CH_3CN)(COR)$]BF_4 yields [$Pd(PPh_3)_2(C_7H_{10}COR)$][$BF_4$] which contains two PPh_3 ligands in a *cis*-orientation around a square planar palladium atom; the 2-acetylnorborn-1-yl residue is in the chelating mode as shown in (82) [66].

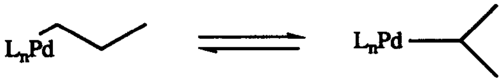
Isomerisations of the alkyl groups attached to Pd(II) complexes [R_2NCS_2]Pd(PR'_3)(alkyl) (R = Me, Et; R' = Et, Ph) (**83**, **84**) have been studied [67].

Syntheses of ortho-palladated azine complexes (85) which show liquid crystalline properties have been reported [68].

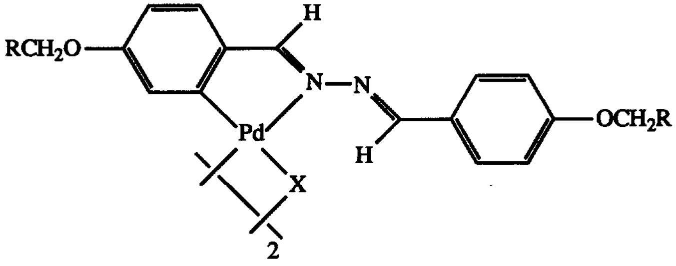


For the phenyl groups,
ipso-C atoms only are shown

(82)

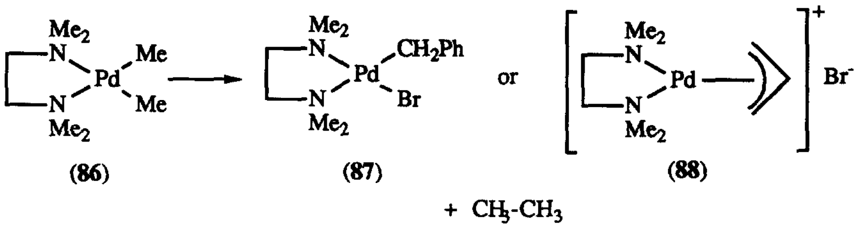


(83) **(84)**

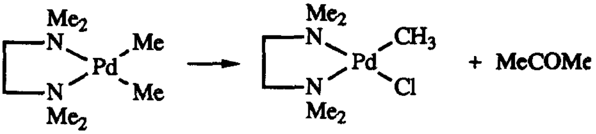


(85)

Pd(Me)$_2$(tmeda) (tmeda = *N,N,N',N'*-tetramethylethylenediamine) **(86)** reacts with aliphatic and aromatic bromides to give homocoupled ethane species and PdBr(η^1-benzyl)(tmeda) **(87)** or [Pd(η^3-allyl)(tmeda)]Br, **(88)**. The reaction with acetylchloride gives the cross-coupled products, acetone and PdClMe(tmeda) **(89)** [69].

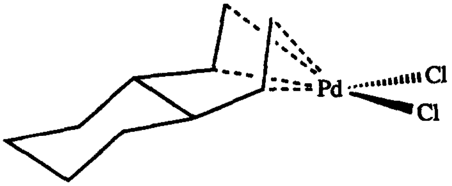


(86) (87) (88)



(89)

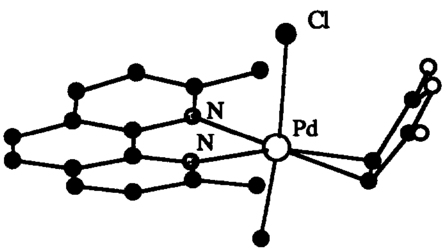
Dichloro(*trans*-η^4-1,2-divinylcyclohexane)palladium, (**90**), a compound containing a non-conjugated diene complexed to Pd has been prepared from the diene and $PdCl_2(PhCN)_2$. The crystal structure of this complex shows the usual square planar geometry of the ligands around the Pd(II) centre with the cyclohexane ring in a chair conformation and the olefinic groups nearly parallel and aligned perpendicular to the coordination plane [70].



(**90**)

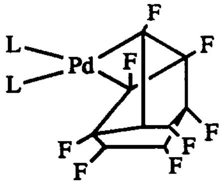
Square planar *cis*-palladium(II) complexes, $[Pd(C_6F_3H_2)_2L_2]$ (L = cod, *N,N,N',N'*-tetramethylethylenediamine, phosphines and phosphites) have been prepared by the reaction of the neutral ligand with $[Pd(C_6F_3H_2)_2(PhCN)_2]$ in chloroform. The conformation around the square planar palladium atom was deduced from their ^{31}P NMR spectra [71].

The steric crowding inherent in the *N,N'*-ligand 2,9-dimethyl-1,10-phenanthroline permits the isolation of the monoolefinic five coordinate Pd(II) complex PdClMe(2,9-dimethyl-1,10-phenanthroline)(η^2-olefin), (**91**). Its preparation and structural characterisation have been described [72].



(91)

2-Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes of palladium(II) **(92)** have been prepared from Pd(0) complexes, Pd(PPh$_3$)$_4$ and *tris*-(dibenzylideneacetone)dipalladium [73].

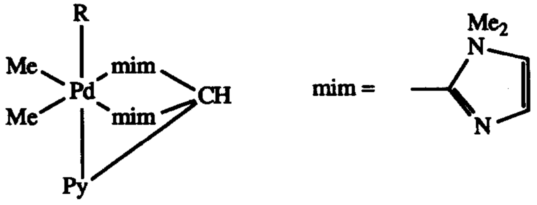


L = t-BuNC; PPh$_3$

(92)

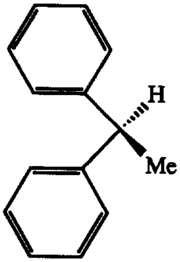
1.3 PALLADIUM (IV)

Pd(IV) complexes containing tripodal nitrogen-donor ligand *bis*(1-methylimidazol-2-yl)(pyridin-2yl)methane, [*fac*-PdRMe$_2$(tripod)]X (R = ethyl, ^{n}propyl, η^1-benzyl and η^1-allyl) **(93)** have been reported [74].



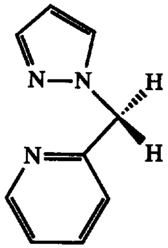
(93)

Neutral benzyl and naphthyl Pd(IV) mononuclear complexes, PdBrMe$_2$(CH$_2$Ar)(L$_2$) (L$_2$ = bpy, phen) have been prepared from dimethylpalladium(II) complexes, PdMe$_2$(L$_2$) by oxidative addition of benzyl and naphthyl bromides [75]. Unstable trimethylpalladium(IV) complexes, *fac*-PdIMe$_3$(L$_2$) with coordinating ligands containing pyridin-2-yl (py), N-methylimidazol-2-yl (mim) and pyrazol-1-yl (pz) units linked by a CH$_2$ or CHMe bridge **(94-97)** have been characterised in solution by NMR spectroscopy [76].



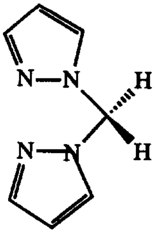
(py)$_2$CHMe

(94)



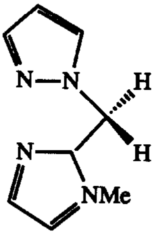
(py)(pz)CH$_2$

(95)



(pz)$_2$CH$_2$

(96)



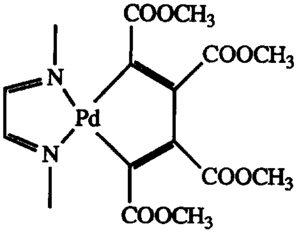
(pz)(mim)CH$_2$

(97)

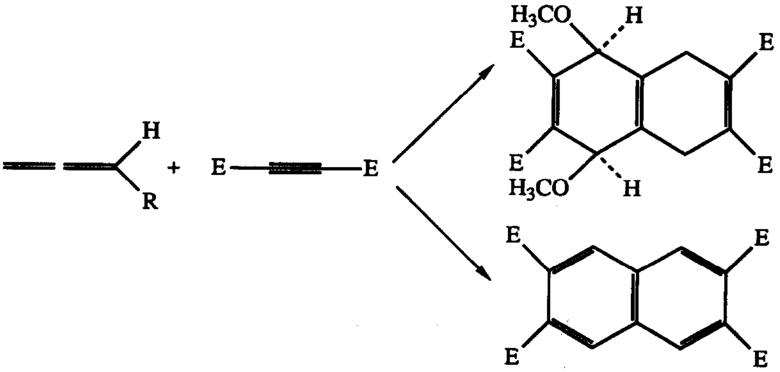
CATALYSIS

1.4 PALLADIUM (0) CATALYSED REACTIONS

A diazadiene palladium(0) complex **(98)** has been shown to catalyse the 2,2-cyclisation of an alkyne with allenes to give naphthalene-2,3,6,7-tetracarboxylic acid derivatives **(99)** [77].



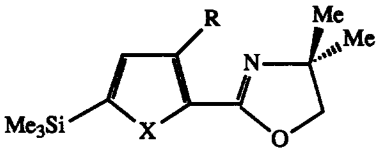
(98)



[E = COOCH$_3$; R = Me, Ph, CH(CH$_3$)OCH$_2$CH$_3$]

(99)

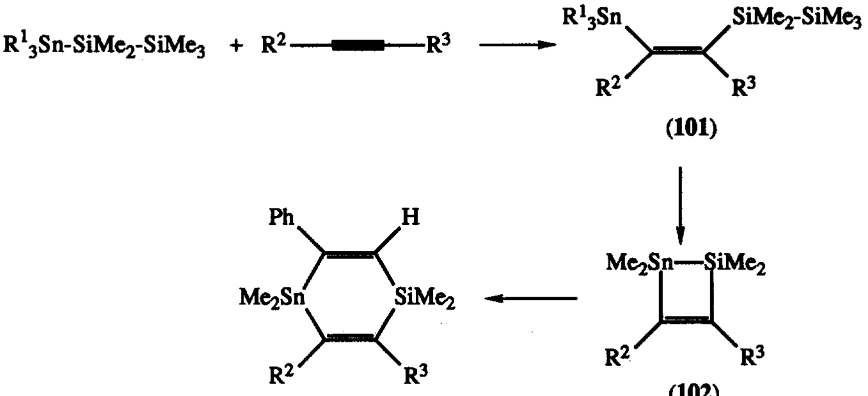
$Pd(PPh_3)_4$ catalyses the coupling reaction of 3-furyllithium intermediates with a variety of aryl-, acyl-, and vinyl halides to yield 3-substituted furans and thiophenes (**100**) [78].



[X = O, S]

(100)

The regio- and stereoselective insertion of alkynes into the Si-Sn bond of disilanylstannanes to give (β–disilanylalkenyl)stannanes (**101-103**) is catalysed by $Pd(PPh_3)_4$ [79]. In such reactions aliphatic alkynes show no reactivity. (β–disilanylalkenyl)stannanes react further with phenylethynes under similar conditions to give organosilicon and organotin compounds.

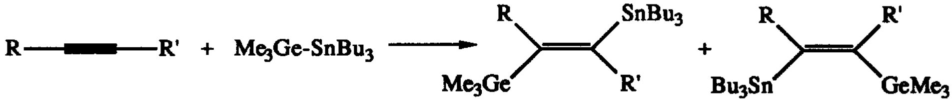


(101)

(102)

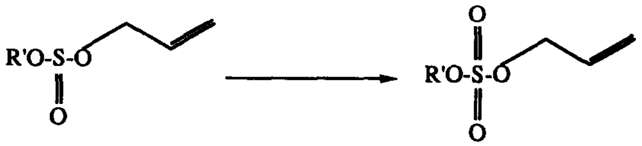
(103)

$Bu_3SnGeMe_3$ adds to terminal alkynes regiospecifically (**104, 105**) in the presence of $Pd(PPh_3)_4$. The distribution of the products depends on the substituents on the alkyne unit [80].



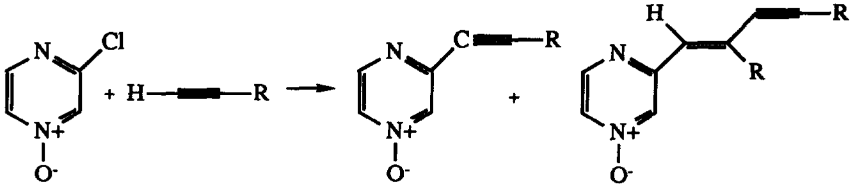
(104) **(105)**

The [2,3]-sigmatropic rearrangement of acyclic and cyclic allylsulfites (**106**) to allylsulfonates (**107**) is catalysed by a Pd(0) species generated from $(dba)_3Pd_2C_6H_6$ and triethylphosphite [81].



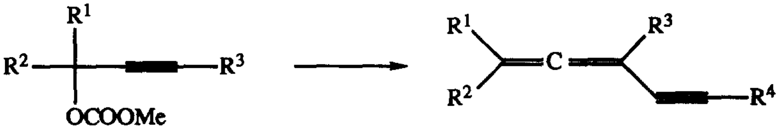
(**106**) (**107**)

$Pd(PPh_3)_2$ catalysed coupling of terminal acetylenes with halo-aromatics has been investigated. For example, the reaction of 3-chloropyroazine-1-oxide with 1-hexyne yields not only the expected 3-(1-hexyne)pyrozine-1-oxide (**108**) but also a co-dimeric product, 3-2-butyl-1-octen-3-ynyl)pyrazine-1-oxide (**109**) [82].



(**108**) (**109**)

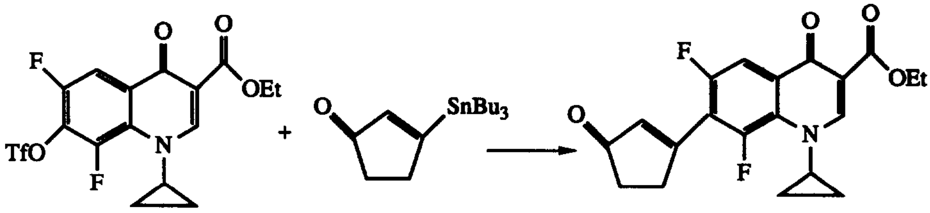
The synthesis of 1,2-dien-4-ynes (**110**) from 2-alkynyl carbonates and terminal acetylenes catalysed by $Pd(PPh_3)_4$ and CuI has been reported [83].



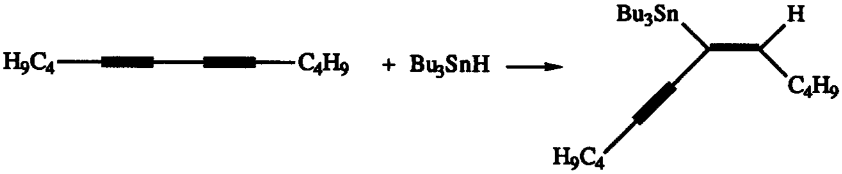
(**110**)

1.5 PALLADIUM (II) CATALYSED REACTIONS

Intermolecular vinylic arylation of cycloalkenes catalysed by $PdCl_2(PPh_3)_2$ has been shown to yield products with complete regio- and chemoselectivity (**111**) [84]. Hydrostannation of alkynes by tributyltinhydride to give vinylstannanes (**112**) stereoselectively (*cis*-addition) is catalysed by $PdCl_2(PPh_3)_2$ [85].

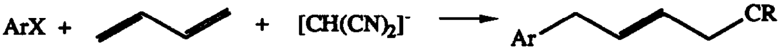


(111)



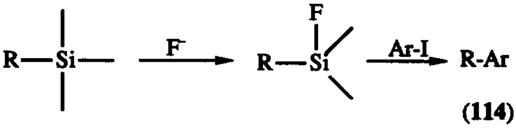
(112)

$PdCl_2(PPh_3)_2$ has been shown to catalyse the 1,4-arylation/alkylation reaction of 1,3-butadiene with halogenoarenes and stabilised anions e.g., $[CH(CN)_2]^-$ (methylcyanoacetate) (113) [86]. Two carbon-carbon bonds are built by a tandem insertion/coupling reaction.



(113)

Cross coupling of organofluorosilicon compounds with aryliodides to give a variety of heteroaromatic compounds (114) is catalysed by $(\eta^3\text{-}C_3H_5PdCl)_2$ [87].

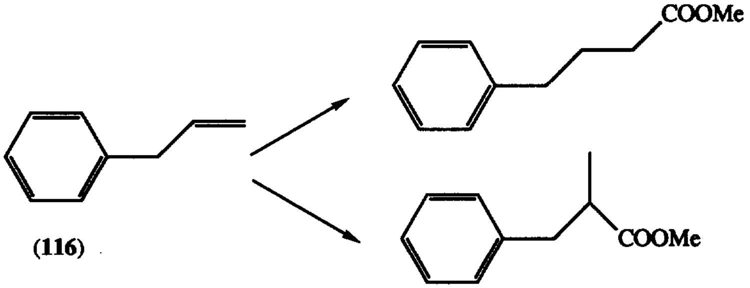


(114)

Synthesis of aromatic acids (115) from benzene, naphthalene or phenanthroline and CO has been reported to be catalysed by $Pd(OAc)_2$ and ^tBuOOH/allyl halides [88].

(115)

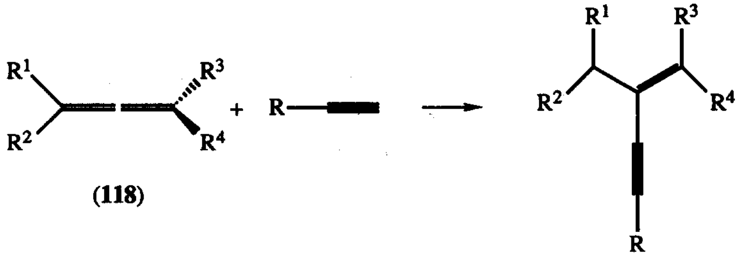
Alkoxycarbonylation of allylbenzenes (**116**) to the corresponding esters (**117**) is catalysed by $PdCl_2(PPh_3)_2$ in the presence of excess phosphine and $SnCl_2.2H_2O$. The reaction is highly regioselective [89].



(116)

(117)

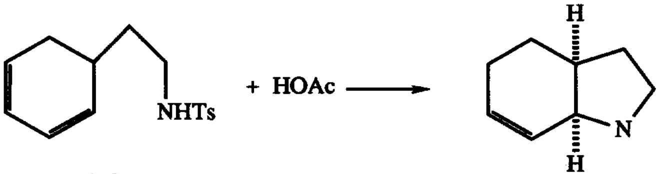
Cross condensation of allenes (**118**) and terminal acetylenes is catalysed by a mixture of $Pd(OAc)_2$ and substituted-aryl phosphines $(R_nC_6H_{6-n})_3P$ (R = OMe; n = 2,3) [90].



(118)

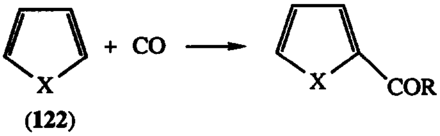
(119)

1,4-Oxidation of 1,3-dienes involving amides (**120**) as nucleophiles leading to the formation of nitrogen heterocycles (**121**) has been shown to be catalysed by $Pd(OAc)_2$ in the presence of LiOAc [91].



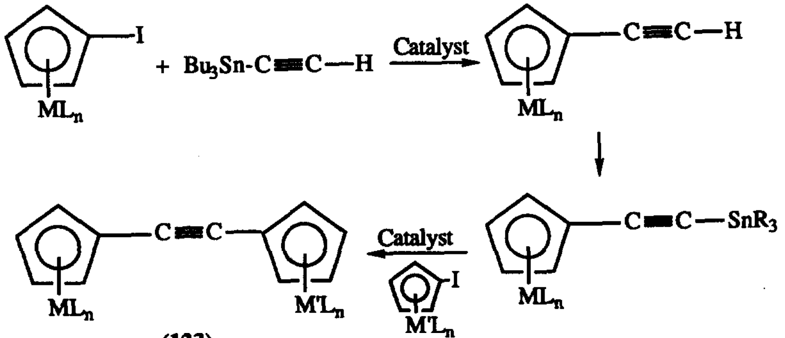
(120)

(121)



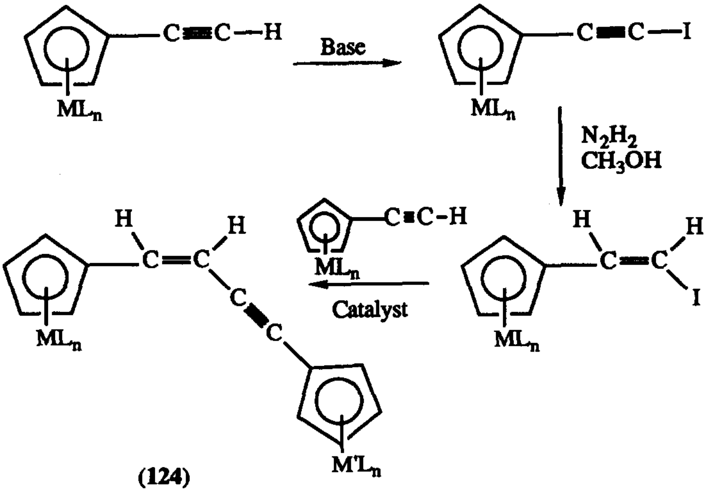
(122)

Palladium acetate catalyses the carboxylation of furan and thiophene **(122)** under low pressures of CO [92]. Sodium acetate and mercury (II) acetate are good cocatalysts for this process. $Pd(CH_3CN)_2Cl_2$ catalyses C-C coupling reactions leading to the formation of hetero-bimetallic complexes **(123, 124)** [93-94]. Selective substitution of the poly(halo)- groups on benzene **(125)** by alkynyl or alkenyl moieties is catalysed by $Pd(PPh_3)_2Cl_2$ **(126)** and $Pd(OAc)_2$ or $Pd(OAc)_2$-PPh_3 mixture **(127)** respectively [95].

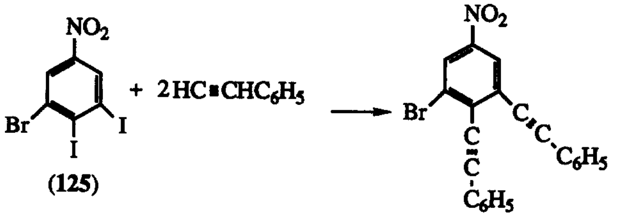


(123)

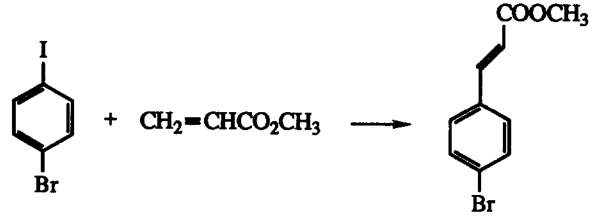
[M, M' = Fe, Mo, W, Mn, Re;
L_n = $(CO)_2CH_3$, $(CO)_3CH_3$, $(CO)_3$]



(124)

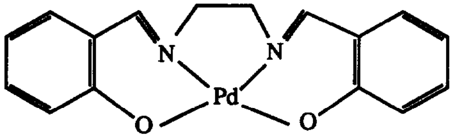


(125) (126)



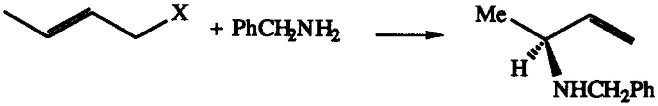
(127)

The catalytic properties of salicylidene ethylenediaminepalladium(II) complex (128) prepared by the reaction of salicylaldiimines with palladium dichloride (and triethylamine as a base) as a hydrogenation catalyst have been investigated [96].



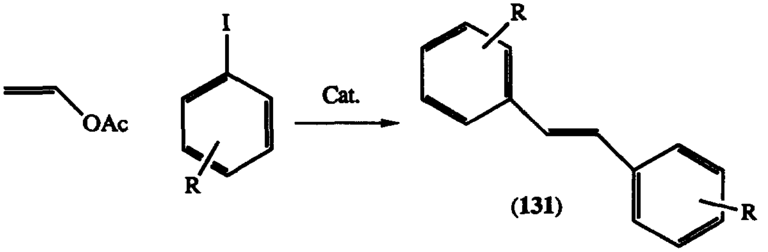
(128)

A chiral ferrocenylphosphine-palladium complex obtained from $Pd_2(dba)_3.CHCl_3$ and (*R*)-*N*-methyl-*N*-*bis*(hydroxymethyl)methyl-1-[(*S*)-1',2-*bis*(diphenylphosphino)ferrocenyl]ethylamine catalyses the asymmetric allylic amination of 2-butenylacetates (129) with benzylamine to give a regio- and stereoselective product, 3-benzyl-amino-1-butene (130) [97].



(129) (130)

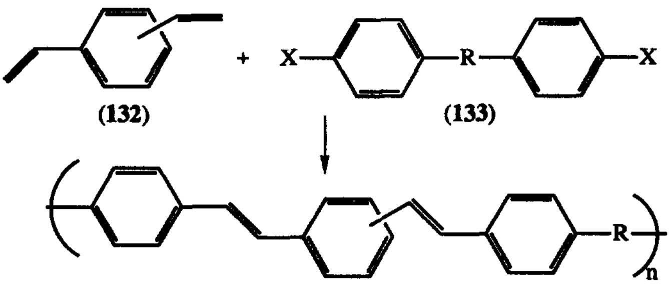
Cross coupling of vinyl acetate to give *trans*-stilbenes (131) is catalysed by interlamellar montmorilloniteethsilyldiphenylphosphinepalladium(II) dichloride [98].



(131)

Cat. =

The reaction between divinylbenzene (**132**) and substituted *bis*(halobenzene) (**133**) to give polymeric species (**134**) is catalysed by palladium acetate and tri-*o*-tolylphosphine (in 1:2 ratio); (**134**) shows liquid crystalline behaviour [99].

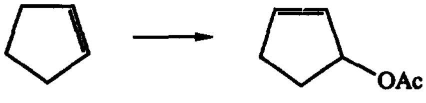


(132) **(133)**

(134)

[X = I, Br; R = $O(CH_2CH_2O)_4$; $O(CH_2)_{12}O$, $O_2C(CH_2)_{10}CO_3$, $(CH_2)_8$, $CO_2(CH_2)_{10}O_2C$]

Conversion of alkenes (**135**) to allylic acetates (**136**) by allylic acetoxylation is catalysed by $Pd(OAc)_2$ in the presence of a MnO_2-benzoquinone mixture which functions as the reoxidation system. Mechanisitic aspects of these reactions have also been discussed [100].



(135) **(136)**

Direct conversion of benzene to phenol with molecular oxygen and CO is catalysed by equimolar mixture of $Pd(OAc)_2$ and 1,10-phenanthroline in acetic acid. Phenyl acetate is obtained as a byproduct in small amounts [101].

$$C_6H_6 + O_2 + CO \longrightarrow C_6H_5OH + CO_2$$

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