Coordination Chemistry Reviews 138 (1995) 195–217

9. Palladium 1992

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CONTENTS

INTRODUCTION

The coordination chemistry of palladium reported during the year 1992 has been reviewed. Although this account does not intend or claim to be comprehensive, examples have been selected to represent important features. Only the primary journals are covered and were searched using BIDS (Bath Information and Data Service) for both palladium (and related) as a keyword and being present in the title. The review covers the chemistry of palladium in its 0 → +4 oxidation states, but does not include the catalytic activity of palladium complexes or complexes containing only Pd-C bonds. Classification of the complexes is according to the oxidation state and donor atom. For complexes containing mixed donor sets the priority ordering P>N>S applies, and neutral donors have priority over charged donor atoms; neutral, mixed donor didentate ligands are treated separately.

9.1 PALLADIUM(IV)

The first examples of fluoro, pseudohalogeno and carbonylatopalladium(IV) complexes have been prepared by exchange of the bromo ligand in [PdBrMe$_2$(CH$_2$Ph)(bpy)] on addition of a silver salt, or silver nitrate and the appropriate anion. The complexes, [PdXMe$_2$(CH$_2$Ph)(bpy)]

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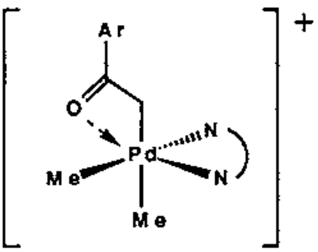
(X = F, Cl, Br, N_3, SCN, OCN, SeCN, O_2CPh, O_2CCF_3), were subsequently employed in a study of the effect of groups X on selective reductive elimination of ethane from the Pd(IV) centre [1].

Low temperature (–5°C) ^1H NMR spectroscopic studies of the oxidative addition of phenacylbromides with [$PdMe_2(L_2)$] (L_2 = bpy, phen) indicated the initial formation of the cations [$PdMe_2(CH_2COAr$-*C,O*)(L_2)] **(1)**, stabilised *via* an intramolecularly coordinated phenacyl group, prior to the formation of the final neutral product *fac*-[$PdBrMe_2(CH_2COAr)(L_2)$] (Ar = Ph, *p*-C_6H_4Br); the structure of *fac*-[$PdBrMe_2(CH_2COPh)(bpy)$] **(2)** was also determined [2].



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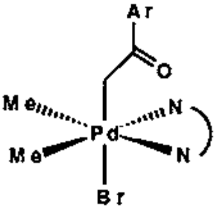
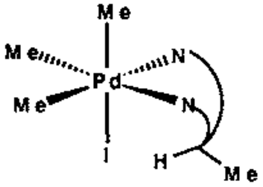


(2)

Low temperature ^1H NMR spectroscopic studies have also revealed that oxidative addition of MeI to [$PdMe_2\{(pz)_2CHMe$-*N,N'*}] (pz = L_2 = pyrazol-1-yl) affords the Pd(IV) complex [$PdIMe_3(L_2)$]. Although two configurations (3) and (4) are possible from *trans* addition of MeI, only (3) was observed as indicated by the large downfield shift of the methine bridgehead proton adjacent to the iodine atom [3].



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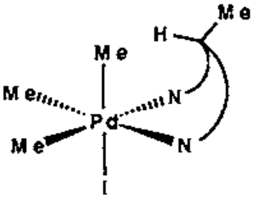

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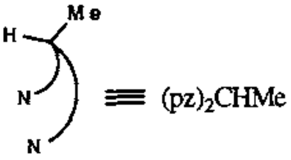
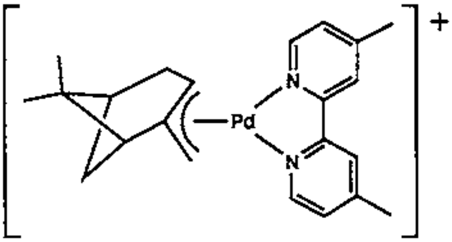


9.2 PALLADIUM(II)

9.2.1 Complexes with phosphine donor ligands

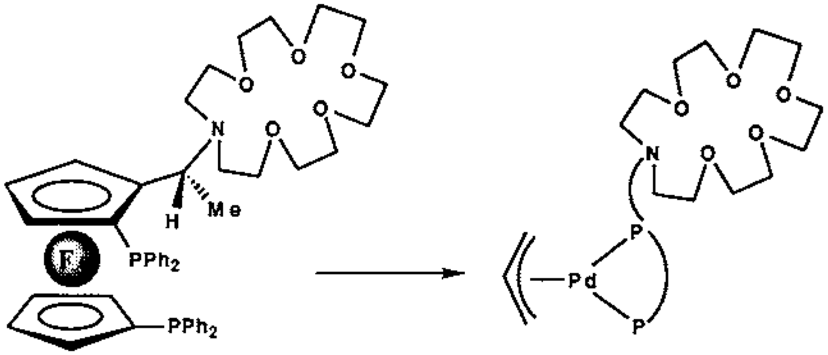
The preparation of the neutral phosphine complexes [$PdClMe(L_2)$] [L_2 = dppe, dppp, dppb and dppf] and the ionic complexes [$PdMe(MeCN)(L_2)]SO_3CF_3$ was reported [4]; the rate of insertion of CO into the Pd-Me bond of the complexes was investigated as a function of the ligand. In a related study, the insertion of alkenes into the Pd-acetyl bonds of [Pd{C(O)Me}Cl(dppp)] and [Pd{C(O)Me}(L$_2$)L')]SO$_3$CF$_3$ (L$_2$ = dppe, dppp, dppb; L' = MeCN, PPh$_3$) as a function of the ligand, the anion and the alkene was explored [5].

The solution state structure of [Pd(η^3-C$_{10}$H$_{15}$){S(-)BINAP}]SO$_3$CF$_3$ based on ^{1}H-2D NOESY and molecular modelling calculations has been presented, and the solid state structure for the model β-pinene allyl complex [Pd(η^3-C$_{10}$H$_{15}$)(4,4'-dimethylbipyridine)](SO$_3$CF$_3$) (5) has been determined by an *X*-ray diffraction study [6].



(5)

A range of chiral ferrocenylphosphine ligands modified by monoaza or diaza crown ethers was synthesised, *eg* (6). Reaction of (6) with di-μ-chloro*bis*(π-allyl)dipalladium(II) produced the π-allylpalladium(II) complex (7) chelated by both phosphorus atoms, leaving the crown ether free. NOE studies on this complex suggested that the aza crown ether group is located at a position suitable to interact with incoming nucleophiles [7].

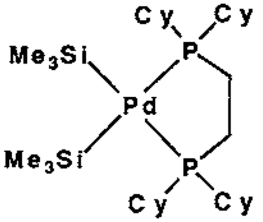


(6)

(7)

The reaction of Pd(0) complexes [Pd(styrene)L$_2$] (L = PMe$_3$, PMe$_2$Ph, PMePh$_2$) with allylic carbonates to afford cationic (π-allylic)palladium complexes possessing alkyl carbonate anions, [Pd(π-allyl)(L$_2$)][OCOOR], was reported. The structure of the hydrolysis product [Pd(η^3-2Me-C$_3$H$_4$)(PMe$_3$)$_2$][OCOOH] was determined from an *X*-ray analysis [8].

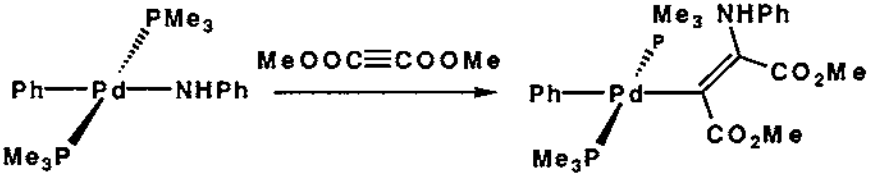
Stable *cis-bis*(silyl)palladium complexes, *eg*. (8), were prepared from the direct reaction of hydrosilanes or 1,2-dihydrosilanes with the dinuclear palladium(I) hydrido complex [Pd(μ-H)(dcpe)]$_2$ [9].



Cy = Cyclohexyl

(8)

Insertion of dimethyl acetylenedicarboxylate into the P-N bond of *trans*-$[Pd\{C_6H_4C(H)=NPh\}(NHPh)(PMe_3)_2]$ and *trans*-$[Pd(Ph)(NHPh)(PMe_3)_2]$ was found to give *cis*- and *trans*-$[Pd\{(MeOOC)C=C(COOMe)(NHPh)\}\{C_6H_4C(H)=NPh\}(PMe_3)_2]$ and *trans*-$[Pd\{(MeOOC)C=C(COOMe)(NHPh)\}(Ph)(PMe_3)_2]$ (**9**) [10].



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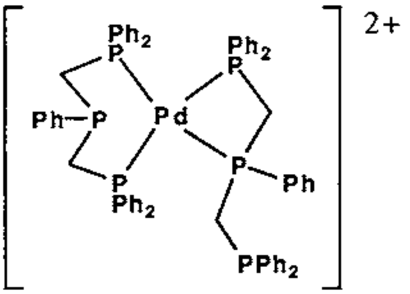
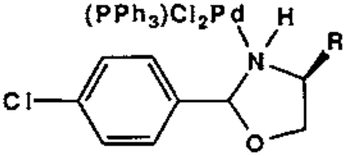
The complexes *trans*-$[Pd(C_7H_{11})_2(L)_2]$ (L = PPh_3, MeCN) have been prepared from the corresponding dihalopalladium(II) salts and 1-lithio-undecafluoro-bicyclo[2,2,1]-heptane. The stability of the Pd-C bond was assessed by examining the reactivity with dilute HCl, NaOH, H_2, O_2 and air [11]. Treatment of $[Pd(NCPh)_2Cl_2]$ with 2 equivalents of dpmp and $[NH_4]PF_6$ yields $[Pd(dpmp)_2](PF_6)_2$ (**10**), the structure of which was solved by a single crystal *X*-ray diffraction study [12]. Complex (**10**) reacts with $[Ir(CO)Cl(EPh_3)_2]$ (E = As, P) to form heterodimetallic cations with luminescent properties.



(10)

A series of optically active complexes of the type *trans*-$[PdCl_2(PPh_3)(oxazolidine)]$ (**11**) has been reported [13]. The synthesis involves metal promoted cyclisation of the optically active

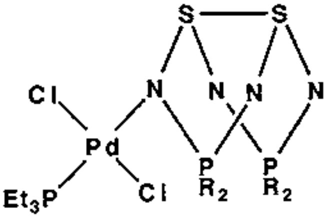
Schiff's bases p-$ClC_6H_4CH{=}NCH(R)CH_2OH$, and proceeds in high chemical and optical yield (de's 78 - 96 %).



R=Me, Et, ^{i}Bu, Bz, Ph

(11)

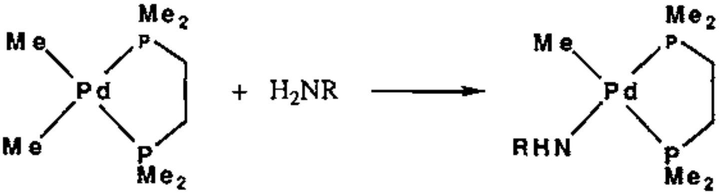
The reaction of the diphosphadithiatetrayocines 1,5-$R_4P_2N_4S_2$ with $[PdCl_2(PEt_3)_2]$ in a 2:1 molar ratio produces the 1:1 adducts *trans*-$[PdCl_2(PEt_3)(R_4P_2N_4S_2)]$ (R = Me, Et) (**12**) in which the $P_2N_4S_2$ ligand is bound to palladium *via* nitrogen [14].



(**12**)

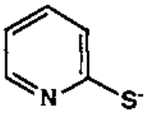
Pyrazolato-bridged dinuclear complexes of the type $[Pd_2X_2(\mu\text{-}L)(PR_3)_2]$ (L = pyrazolato, 3,5-dimethylpyrazolato; X = Cl, Br, I; PR_3 = PBu_3, PMe_2Ph) have been prepared, and the structure of $[Pd_2Cl_2(\mu\text{-}L)(PMe_2Ph)_2]$ (L = 3,5-dimethylpyrazolato) determined by single crystal *X*-ray diffraction [15]. Interestingly, the polydentate pyrazolyl donor ligand [HB(3-^{t}Bu-pyrazolyl)$_3$] reacts with $[Pd(Ph)(Br)(PMe_3)_2]$ to afford a complex in which the ligand adopts a monohapto coordination mode in the solid and solution state [16].

Reaction of amides ($RCONH_2$ and $CF_3SO_2NH_2$) with $[PdMe_2(L_2)]$ (L_2 = $2PEt_3$, dcpe, dmpe) to yield new complexes containing palladium-amido nitrogen bonds has been reported [17], *eg*. (**13**).



R= SO_2CF_3 (**13**)

The potentially didentate N/S-donor ligand (**14**) has been employed to prepare a range of mononuclear complexes exhibiting various coordination modes, including chelation (**15**), Sunidentate (**16**) and exchange between the two. The solution state behaviour of the complexes was examined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies, and the solid state structure of $[PdCl(pyS)(PPh_3)]$ (py = 2-pyridyl) determined [18].



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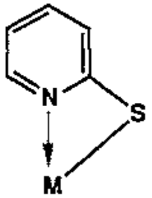

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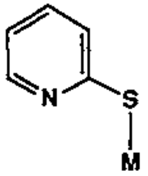
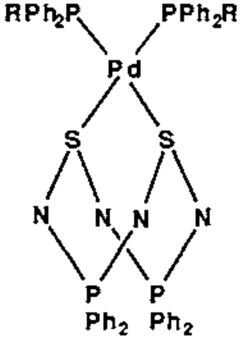


(16)

The preparation of $[Pd(PPh_3)_2(1,5\text{-}Ph_4P_2N_4S_2)]$ and $[Pd(PPh_2Me)_2(1,5\text{-}R_4P_2N_4S_2)]$ (R = Ph, Et) from $[Pd(L)_4]$ (L = PPh_3 or PPh_2Me) and $1,5\text{-}R_4P_2N_4S_2$ has been reported [19]. The heterocyclic ligand in these complexes is bonded to palladium in an η^2-S,S' fashion (**17**). Mild heating of the monomers, in the solution or solid state, affords the dimers $[Pd(PPh_2R')(1,5\text{-}R_4P_2N_4S_2)]_2$ (R = R' = Ph; R' = Me, R = Ph, Et). Reaction of the anion $Ph_4P_2N_4S_2Me^-$ with *cis*- or *trans*-$[PdCl_2(PEt_3)_2]$ gives the complex $[PdCl(PEt_3)_2(Ph_4P_2N_4S_2Me)]$ (**18**), exhibiting a Pd-S σ-bond [20].



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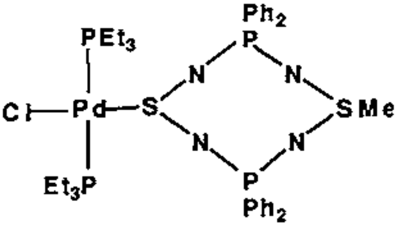
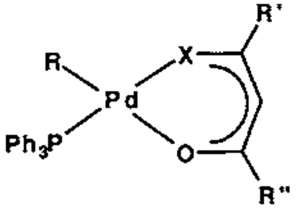


(18)

The mononuclear complex $[Pd(SR)_2(dppe)]$ (R = C_5H_9NMe) is formed on reaction of $[PdCl_2(dppe)]$ with NaSR (R = 4-mercapto-1-methylpiperidine). Subsequent reaction with further $[PdCl_2(dppe)]$ produced the dimeric cationic complex $[Pd(\mu\text{-}SR)(dppe)]_2^{2+}$. The single crystal X-ray structures of the monomer and dimer were reported [21]. Similar dinuclear palladium(II) complexes of the form $[PdCl(\mu\text{-}EAr)(PR_3)]_2$ (E = S, Se, Te; Ar = Ph, p–C_6H_4OMe, p–C_6H_4OEt; PR_3 = PBu_3, PMe_2Ph) have also been prepared and characterised [22].

Two series of μ-hydroxy-bridged complexes $[Pd(\mu\text{-}OH)L_2]_2(BF_4)_2$ (L = PPh_3, PPh_2Me) and $[Pd(\mu\text{-}OH)(L\text{-}L)]_2(BF_4)_2$ (L-L = dppe, dcpe) have been synthesised by treating the corresponding dichloropalladium(II) phosphine complexes with $AgBF_4$ in aqueous acetone solution [23]. Reaction of $[PdCl_2(L_2)]$ (L_2 = dppm, dppe, dppp) with methyltriflate affords the triflate complexes $[Pd(OTf)_2(L_2)]$ [24].

The preparation of methyl and phenyl complexes of the general formula $[PdR(\beta\text{-dik})(PPh_3)]$ (**19**) (R = Me, Ph; β-dik = β-diketonato or monothio-β-diketonato) and insertion of CO into the Pd-C bond to form the corresponding acyl complexes has been reported [25].

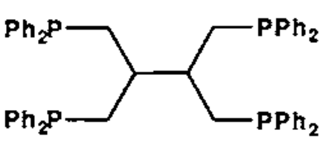


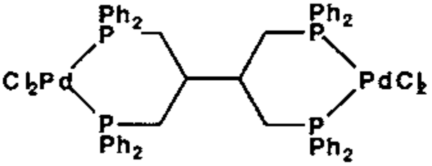
X = O, S; R=Me, Ph

R'=R"=Me, CF_3, Ph

(**19**)

The tetra-tertiary phosphine (**20**) has been prepared, and reacts to form complexes $[CH(CH_2PPh_2)_2PdX_2]_2$ (**21**) (X = Cl, Br, I) [26]. The coordination mode was confirmed by a single crystal *X*-ray diffraction study on $[CH(CH_2PPh_2)_2PdCl_2]_2$.

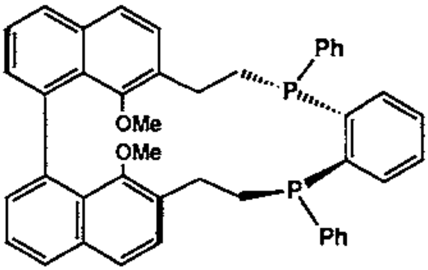




(**20**)

(**21**)

A series of 16- and 18-membered diphospha-macrocycles has been synthesised, *eg*. (**22**), and their coordination chemistry with $[PdCl_2(MeCN)_2]$ studied [27].



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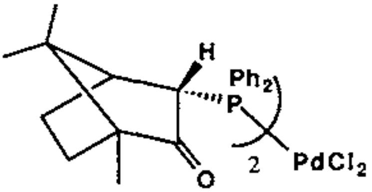
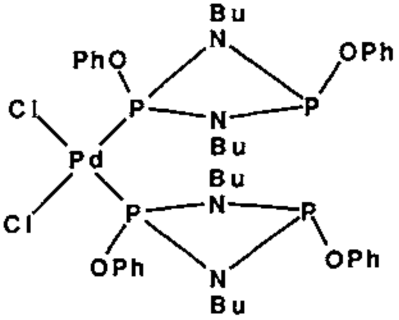


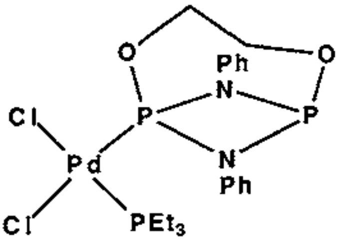
(**23**)

Reaction of *endo*-3-diphenylphosphino-(IR)-(+)-camphor with $[PdCl_2(NCPh)_2]$ affords $[PdCl_2(L)_2]$ (**23**) as a *cis-trans* mixture in solution. The *X*-ray crystal structure of the *cis*- form has been determined [28].

Reaction of the cyclodiphosphazane *cis*-$[^tBuNP(OPh)]_2$ (L) with $[PdCl_2(COD)]$ affords mononuclear complexes *cis/trans*-$[PdCl_2L_2]$ in which the cyclodiphosphazane acts as a monodentate ligand through phosphorus (**24**) [29]. Bicyclodiphosphazenes react with $[Pd_2Cl_4(PEt_3)_2]$ to yield mononuclear (**25**) and dinuclear (**26**) complexes in which the ligand is bound through P in monodentate or bridging didentate fashion [30].



(**24**)



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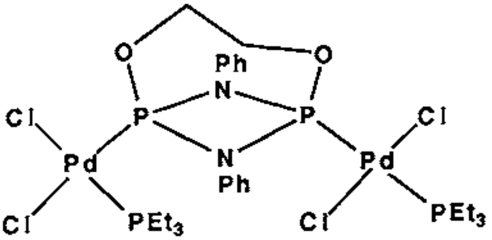


(**26**)

9.2.2 *Complexes with nitrogen donor ligands*

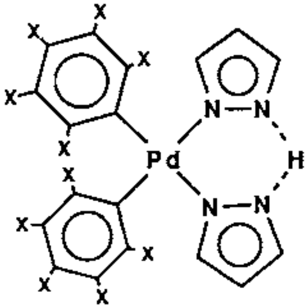
The diorganomercurial $[HgR_2]$ (R = $C_6H(CHO)$-6-$(OMe)_3$-2,3,4] reacts with $[Pd_2Cl_6]^{2+}$ or $[PdCl_4]^{2-}$ to give an aqueous solution containing the dinuclear complex $[PdRCl(\mu\text{-}Cl)]_2$. Addition of bpy or phen to this solution leads to isolation of the complexes [PdRCl(bpy)] and [PdRCl(phen)], and from dichloromethane extracts the cyclometallated complex $[Pd(\eta^2\text{-}R')(\mu\text{-}Cl)]_2$ containing the rearranged ligand R' = $C_6H(CHO)$-2-$(OMe)_3$-3,4,5 can be isolated. Addition of bpy or phen to this complex affords [PdR'Cl(bpy)] and [PdR'Cl(phen)]. Reaction of these monoorgano-halogeno complexes with a variety of silver(I) salts produced a range of cations [31].

The synthesis of cationic η^3-palladium(II) cations containing a range of 2,9-disubstituted 1,10-phenantholines (L), [Pd(η^3-2-Butenyl)(L)]$^+$ has been reported. The proportion of molecules exhibiting the allyl unit in an *anti* configuration (**27**) was determined as a function of the phenanthroline substituent [32].

(**27**)

A series of benzylpalladium complexes [PdX(CH$_2$Ph)(bpy)] (X = Br, N$_3$, SCN and O$_2$CPh) has been prepared by reductive elimination from the corresponding Pd(IV) complexes [PdXMe$_2$(CH$_2$Ph)(bpy)]. Reductive elimination from analogous Pd(IV) centres with X = F, Cl, I, OCN, SeCN, O$_2$CCF$_3$ gave a 9:1 mixture of [PdX(CH$_2$Ph)(bpy)] and [PdXMe(bpy)]. The crystal structure of [PdN$_3$(CH$_2$Ph)(bpy)] was determined [33].

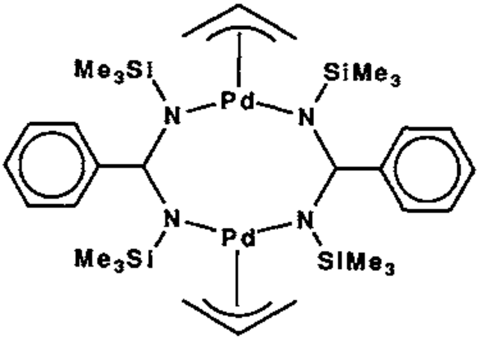
The reaction of [PdR$_2$(PhCN)$_2$] (R = C$_6$F$_5$, C$_6$Cl$_5$) and [{Pd(C$_6$F$_5$)$_2$(μ-Cl)}$_2$]$^{2-}$ with L-H (L-H = pyrazole or 3,5-dimethylpyrazole) gives complexes of the form [PdR$_2$(L-H)$_2$] and [Pd(C$_6$F$_5$)$_2$Cl(L-H)]$^-$. Treatment of [PdR$_2$(L-H)$_2$] (R = C$_6$F$_5$, C$_6$Cl$_5$; L-H = pyrazole) with NBu$_4$OH leads to the formation of the pyrazole-pyrazolato complexes [PdR$_2$(L)(L-H)]$^-$, exhibiting identical pyrazolyl rings (**28**), as determined by IR and NMR spectroscopy and an *X*-ray diffraction study of (**28**) (X = F) [34].



(**28**) X=Cl or F

The dimeric complex [Pd(η^3-C$_3$H$_5$){PhC(NSiMe$_3$)$_2$}]$_2$ (**29**) has been prepared from the reaction of [Pd(η^3-C$_5$H$_5$)Cl]$_2$ with Li[PhC(NSiMe$_3$)$_2$]. Under controlled hydrolysis (**29**) yields the benzamidinate bridged dimer [Pd(η^3-C$_3$H$_5$){PhC(NH)$_2$}]$_2$, whose solid state structure has been determined [35].

Palladium(II) complexes [Pd(L)$_2$]Cl$_2$.H$_2$O and [Pd$_3$(L)$_4$Cl$_2$]Cl$_4$.H$_2$O (L = 1-thia-4,7-diazacyclononane) have been prepared and characterised by *X*-ray crystallography. The mononuclear complex [Pd(L)$_2$]Cl$_2$.H$_2$O (**30**) is coordinated by the N-donor atoms of the ligand, while the trinuclear species consists of a central [Pd(L)$_2$]$^{2+}$ unit bridged *via exo* coordination of its thioether groups to two [Pd(L)Cl]$^+$ fragments [36].



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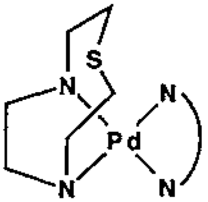

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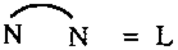
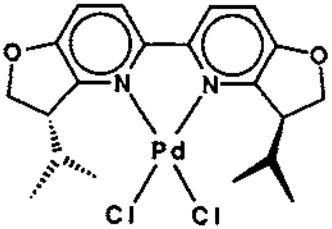
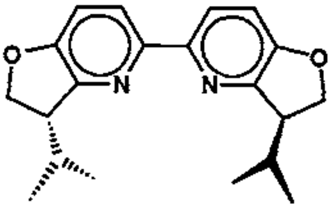


A series of palladium phenoxide complexes $[Pd(OPh)_2L_2]$ [L_2 = tmed, $(pyrrolidine)_2$, $(N\text{-}methylpyrrolidine)_2$] and $[Pd(OPh)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ has been synthesised, with characterisation paying particular attention to the role of both N-H---O and O-H---O hydrogen bonding in the resulting structures. The single crystal *X*-ray structures of the complexes $[Pd(OPh)_2(pyrrolidine)_2]$ and [Pd(OPh)(NCN)] were determined [37].

The palladium(II) complex (31) was prepared from the optically active, 2,2'-bipyridyl ligand (*S*,*S*)-(32). Coordination of the ligand *via* both pyridyl nitrogens was indicated by NMR spectroscopic and FAB MS evidence [38].



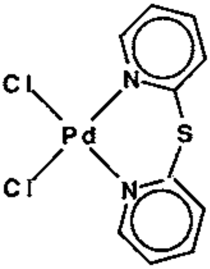
(31)



(S,S)-(32)

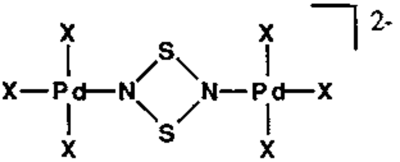
A single crystal *X*-ray structure analysis of $[PdCl_2(bpy)]$ has shown the planar $[PdCl_2(bpy)]$ units to be stacked in columns along the *c* direction [39]. The synthesis and characterisation of three series of *cis*-dichloropalladium complexes containing 4,4'-disubstituted bipyridyl ligands has been reported [40].

The di-2-pyridyl sulfide (dps) containing complexes [$PdCl_2$(dps)] (**33**) and [Pd(MeOdiene)Cl(dps)] (MeOdiene = $MeOC_8H_{12}$, $MeOC_{10}H_{12}$) have been synthesised by reaction of dps with [$PdCl_2$(diene)] and $[Pd(MeOdiene)(\mu\text{-}Cl)]_2$ respectively. The reaction of dps with the anions $[Pd(diene)(acetone)_2]X_2$ and $[Pd(MeOdiene)(acetone)_2]X$ has also been explored. The dynamic behaviour of some of the complexes in solution was studied by NMR spectroscopy [41].

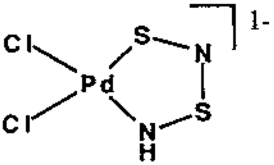


(**33**)

The compound S_4N_4 reacts with $[PPh_4]_2[Pd_2X_6]$ (X = Cl, Br) to give a mixture of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)X_6]$ (**34**), $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)X_4]$ and $[PPh_4]_2[Pd(\mu\text{-}S_2N_2H)\ X_2]$ (**35**). The single crystal *X*-ray structures of (**34**) (X = Cl, Br) and (**35**) were reported [42].

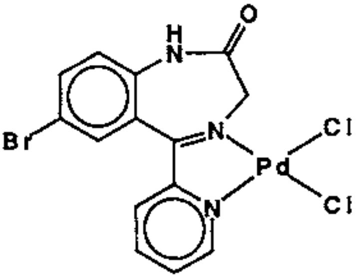


(**34**)



(**35**)

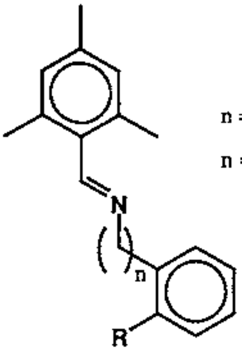
The dichloropalladium(II) complex of bromazepam (**36**) has been prepared, and its structure determined. The kinetics of displacement of bound bromazepam by 1,10-phenatholine and 2,2'-bipyridine have been studied by stopped-flow spectrophotometry [43]. The kinetics of the substitution reaction between anions $S_2O_3^{2-}$, SCN^-, Br^-, I^- and the palladium(II) complex $[Pd(N\text{-}N\text{-}N)X]^+$ (*N-N-N* = *N*-alkyl-diethylene-triamine) has also been investigated [44].



(**36**)

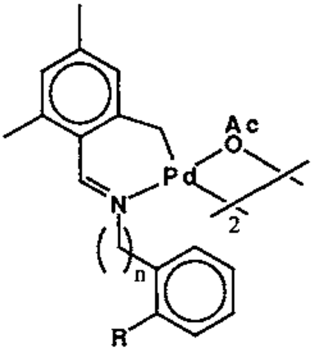
9.2.3 Cyclometallation Complexes

Reaction of the imines (**37**) with $Pd(OAc)_2$ in refluxing acetic acid affords cyclometallated complexes containing an aliphatic M-C bond (**38**) in preference to metallacycles with an aromatic M-C bond. Compounds of the latter type were obtained, however, from (**37**: n = 1) and $Pd(OAc)_2$ under milder conditions, but isomerise to (**38**: n = 1) in refluxing acetic acid. Cyclometallated complexes containing an aromatic M-C bond were also obtained from the action of $Pd(OAc)_2$ on (**39a,b**), but (**39c**), under identical conditions, gave a cyclopalladated species possessing an aliphatic M-C bond (**40**) [45]. In a separate report, the crystal structure of (**41**) was determined [46].

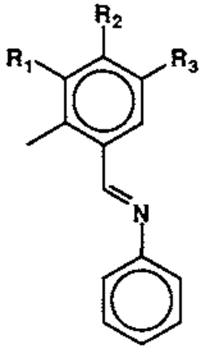


n = 0, 1, 2; R=H
n = 1; R=Me

(37)

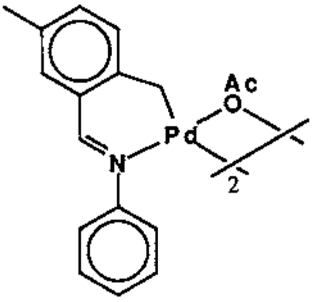


(38)



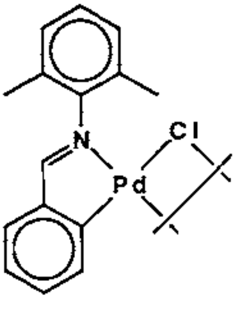
a : R_1=H; R_2=Me; R_3=H
b : R_1=Me; R_2=MeO; R_3=H
c : R_1=R_2=H; R_3=Me

(39)

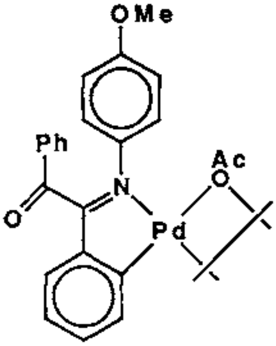


(40)

The reaction of $[Pd(OAc)_2]$ with *N*-(4-methoxyphenol)-α-benzoylbenzylideneamine has been reported to give two different acetate bridged, orthopalladated complexes (**42**). The two diastereoisomeric complexes differed only in the dihedral angle between the PhC=O and PhC=N planes, as established from *X*-ray diffraction data [47].

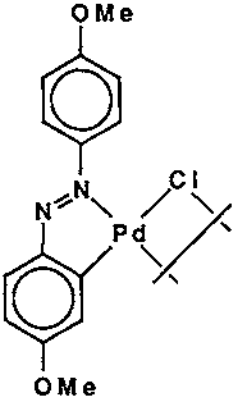


(41)

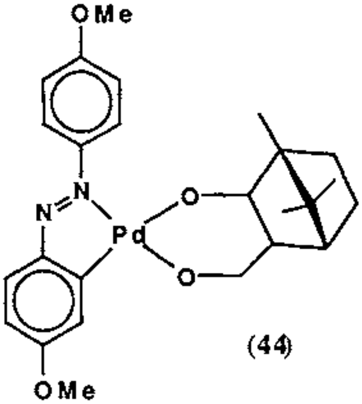


(42)

Reaction of chloro-bridged cyclopalladated complexes, *eg*. (43), and the optically pure salt K[(R)-(+)-hydroxymethylene camphor] gave the corresponding monomers (**44**). Circular dichroism data indicate diastereoisomeric mixtures consisting of two complexes with the 7,7'-dimethyl bridge being above or below the palladium coordination plane [48].

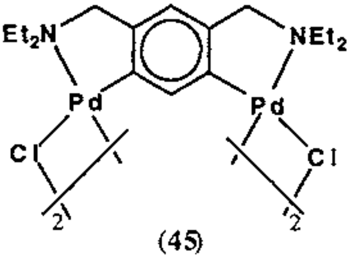


(43)



(44)

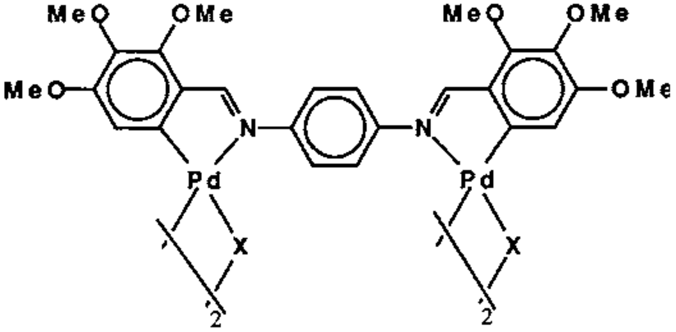
Doubly cyclopalladated complexes derived from 1,3-disubstituted phenyl-amines and -imines have been prepared. Metallation in both cases occurs with regio-specificity at the 4,6-phenyl positions (45) [49,50]. Bridged splitting reactions of (**45**) wth a variety of reagents was reported [49].



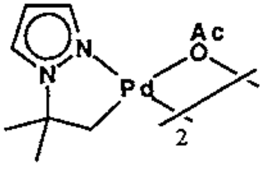
(45)

Treatment of 1,4-phenyl-*bis*(benzylidene amine) ligands with either $Pd(OAc)_2$ followed by NaX (X = Cl, Br), or $PdCl_2$ followed by LiBr, afforded the tetranuclear complexes (46). The single crystal *X*-ray structure of (46) (R = Cl) was determined [51].

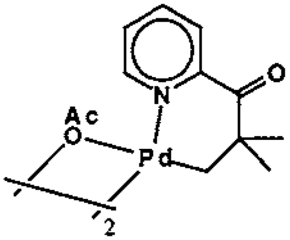
The preparation of $[Pd(bpyMe\text{-}H)(H_2O)_2]^{2+}$ (bpyMe-H = 1-methyl-2,2'-bipyridin-3-yl-ium), $[Pd(bpyMe\text{-}H)(ON_2O)_2]$ and $[Pd(bpyMe\text{-}H)(H_2O)(ON_2O)]ClO_4$ has been reported [52]. For 3-aryl-1-methylpyrazoles, cyclopalladated complexes possessing an aryl M-C bond were synthesised [53], whilst di- and tri-nuclear cyclometallated species containing an alkyl M-C bond could be prepared from 1-^{t}Bu-pyrazole and $Pd(OAc)_2$ (47) [54]. The reaction of 2-pivaloylpyridine and $Pd(OAc)_2$ also gives a cyclometallated species containing an alkyl M-C bond (48) [55].



(46) X = Cl, Br

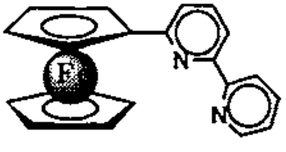


(47)

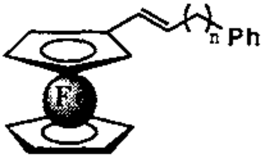


(48)

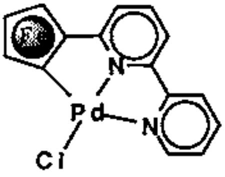
Ferrocenyl based *N*-donor ligands have also been employed in cyclopalladation reactions. Thus, reaction of ligands such as (49) with $[PdCl_2(cod)]$ [56] or (50) with $Na[CH_3CO_2]/Na[PdCl_2]$ [57] affords cyclometallated products in which a Pd-C bond is formed to the cyclopentadienyl ring. The single crystal *X*-ray structure of (51) was reported [56].



(49)

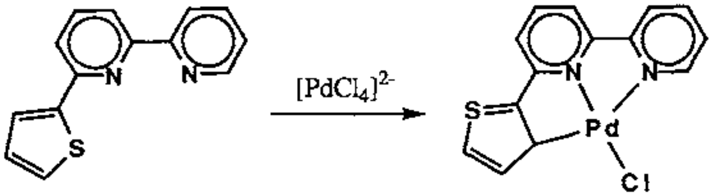


(50) n=1, 2



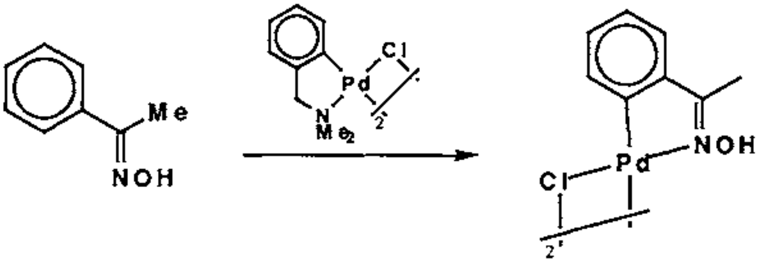
(51)

The potentially *N,S*-didentate ligand 2-(2'-thienyl)pyridine and the *N,N',S*-tridentate ligand 6-(2-thienyl)-2,2'-bipyridine react with $Pd(OAc)_2$ or $[PdCl_4]^{2-}$, respectively, to give complexes in which the thienyl ring is metallated at the 3-position, *eg*. (**52**) [58,59]. However, under mild conditions, the tridentate ligand yields a non-metallated product [59].

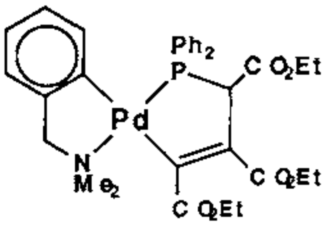


(**52**)

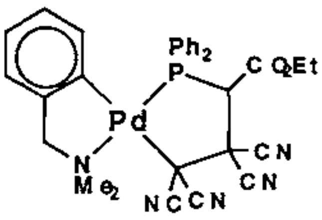
In an interesting report, a series of *ortho*-palladated complexes $[PdCl\{C_6H_4(CR{=}NOH)\text{-}2\}]_2$ (R = H, Me, Et, Ph) was prepared *via* ligand-exchange reactions between acyl oximes and cyclopalladated complexes of *N,N*-dimethylbenzylamine, {(dimethylamino)methyl}ferrocene or benzophenone oxime [60]. An example is the preparation of (**53**) from $C_6H_5(CMe{=}NOH)\text{-}2$ and $[PdCl\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$. The metallated dimers were subsequently converted into monomers by reaction with a variety of pyridines, and the *X*-ray crystal structures of four such derivatives of (**53**) were elucidated [60].



(**53**)



(**54**)

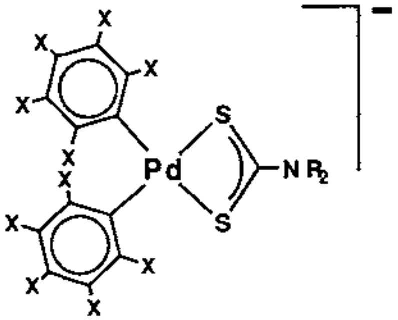


(**55**)

The reaction of the palladium enolate complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)\{Ph_2PCH{=}C(O)Et\}]$ with $Me_2OCC{\equiv}CCO_2Me$ and $(NC)_2C{=}C(CN)_2$ has been reported to give the alkenyl complex (**54**) and the alkyl complex (**55**) [61].

9.2.4 *Complexes with sulfur donor ligands*

The reaction of phenylglyoxylic acid with $Pd(OAc)_2$ in the presence of Bu_2S gave the dinuclear oxalate bridged complex $[\{Pd(Ph)(Bu_2S)\}_2(\mu\text{-}C_2O_4)]$ [62]. The hydroxo-complexes $[NBu_4]_2[\{Pd(C_6X_5)_2(\mu\text{-}OH)\}_2]$ (X = Cl, F) react with amines in the presence of carbon disulfide to give the corresponding dithiocarbamate complexes (**56**). Structural assignment was based on conductance measurements and spectroscopic methods (IR, ^1H and ^{19}F NMR) [63].



R = Me, Et

X = Cl, F

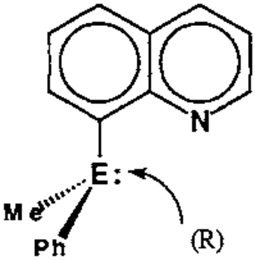
(56)

The kinetics of complex formation between $Pd(H_2O_4)^{2+}$ and the thioethers Me_2S, Et_2S, 1,4-dithione and 1,4-thionane have been investigated as a function of temperature and pressure by use of stopped-flow and conventional spectrophotometry [64].

The synthesis and spectroscopic characterisation of $[Pd\{Te(CH_2)_4\}_2X_2]$ (X = Cl, Br, I) has been reported. The complexes adopt a *trans*-configuration, and the structure of *trans*-$[Pd\{Te(CH_2)_4\}_2Cl_2]$ was confirmed by an *X*-ray analysis [65].

9.2.5 *Complexes with mixed donor ligands*

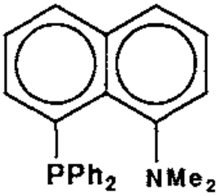
The preparation of square-planar and square-pyramidal palladium(II) complexes $[Pd(L)_2](PF_6)_2$ and $[PdCl(L)_2]X$ (L = (±)-methylphenyl(8-quinolyl)arsine, (±)-methylphenyl(8-quinolyl)phosphine (**57**); X = Cl, PF_6) has been reported. Complexes were prepared in enantiomerically and diastereomerically homogeneous forms, and their behaviour in solution has been studied by variable temperature NMR spectroscopy [66].



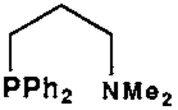
E = As

E = P (**57**)

Using the mixed *P,N*-donor ligands *PAN* (**58**) and *PC_3N* (**59**) the synthesis of a range of palladium(II) complexes has been described: $[PdCl_2(PAN)]$, $[PdCl_2(PAN)_2]$, $[PdMe(PAN)]Y$ ($Y^- = Cl^-, SO_3CF_3^-, BF_4^-$), $[PdMe(PAN)(MeCN)]Y$ ($Y^- = SO_3CF_3^-, BF_4^-$), $[PdMeCl(PC_3N)]$ and $[PdMe(PC_3N)(MeCN)](SO_3CF_3)$. Investigations on these complexes focused mainly on the carbonylation of the M-C bond, and for $[PdCl_2(PAN)_2]$ and $[PdMeCl(PAN)]$ single crystal *X*-ray structure determinations were carried out [67].

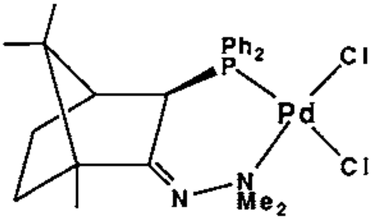


PAN (**58**)

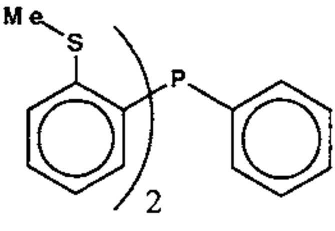


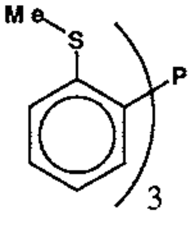
PC_3N (**59**)

Treatment of the *Z*-*exo*-phosphine $PPh_2C_{10}H_{15}NNMe_2$ with $[PdCl_2(NCPh)_2]$ or $Na[PdCl_4]$ affords the complex (**60**). The further reaction of (**60**) with a variety of reagents (*eg.* LiBr and NaI) was reported, along with the single crystal *X*-ray structure of (**60**) [68].



(**60**)



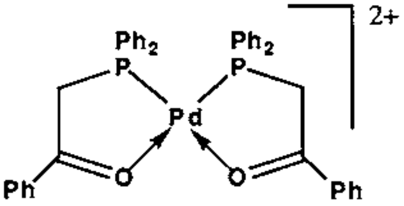


(**61**) (**62**)

A series of palladium complexes containing the chelate ligands (**61**) and (**62**) have been synthesised. The potentially tridentate ligand (**61**) acts as a *P,S*-chelate, forming complexes $[Pd\{PPh(C_6H_4SMe\text{-}o)_2\}X_2]$ (X = Cl, Br, I), whilst (**62**) forms square planar complexes $[Pd\{PPh(C_6H_4SMe\text{-}o)_2\}](ClO_4)_2$ with coordination again through one phosphorus and one sulfur of each ligand. Further, the *X*-ray crystal structure of the latter shows the two coordinated S-Me groups to be mutually *cis* [69].

The reaction between bis(μ-chloro)bis{(*R*)-1-[(dimethylamino)ethyl]naphthylenyl-C^2,*N*}-dipalladium(II) and the didentate *P,S*-donor ligand $Ph_2PCH_2CH_2SMe$ affords a pair of internal diastereomeric complex cations arising from the coordinated sulfur stereocentre. The solid state structure of the diastereomeric mixture has been determined, and its behaviour in solution studied by variable temperature NMR spectroscopy [70].

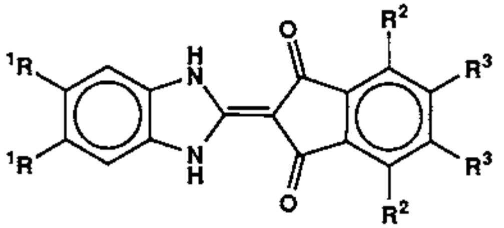
Diphenylphosphinoacetone, Ph_2PCH_2COMe (HL), and its enolate anion , L^-, have been used to prepare the complexes *trans*-$[PdCl_2(HL)_2]$ and *cis*-$[Pd(L)_2]$, which were characterised by IR and NMR spectroscopy. A single crystal *X*-ray diffraction study of $[PdCl_2(HL)_2]$ revealed the expected square planar geometry for palladium [71]. In a related report, treatment of *cis*-$[Pd\{Ph_2PCH{=}C(O)Ph\text{-}P,O\}_2]$ with HBF_4/H_2O afforded the cationic complex *cis*-$[Pd\{Ph_2PCH_2C(O)Ph\text{-}P,O\}_2](BF_4)_2$ (**63**), whilst treatment with commercial $BF_3{\cdot}Et_2O$ gave *cis*-$[Pd\{Ph_2PCH_2C(O)Ph\text{-}P,O\}_2](BF_4)[B_2H_7]$ (structure determined) [72].



(63)

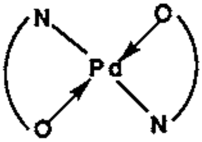
Two series of palladium(II) complexes, $[Pd(qo)_2]$ and $[Pd(qo)Cl]_2$, containing the anion of *o*-benzoquinone-2-oximes (qo) have been synthesised [73]. The *N,O*-chelating ligands (**64**), LH, react to give the palladium(II) c

omplexes $[Pd(L)_2]$ (**65**) and $[PdCl(L)(PR_3)]$, and for $[PdCl(L^*)(P^nBu_3)]$ the solid state structure was determined [74].



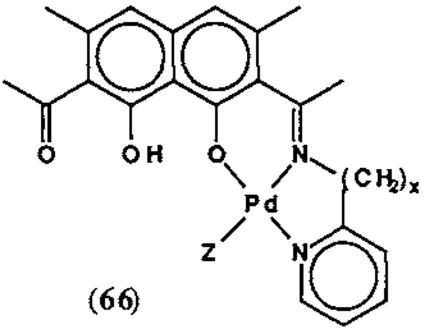
(64)

$L^* = R^1 = R^2 = R^3 = H$



(65)

The 2-substituted phenanthroline ligands 2-(2,5-dimethoxyphenyl)-1,10-phenanthroline and 2-(2,5-dihydroxyphenyl)-1,10-phenanthroline react with palladium(II) salts to form complexes exhibiting *N,O',O''*-coordination [75]. Coordination *via* the *N,O',O''*-donor set was also found for complexes (**66**) [76].

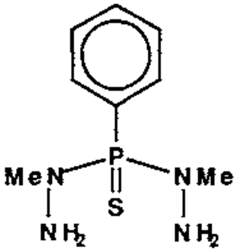


(66)

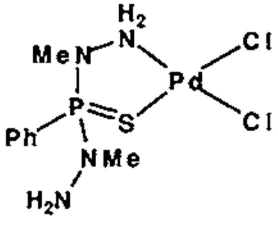
X	Z
1	Cl
2	Cl
3	N_3

The reaction of methyl 2-pyridyl ketone with $Li_2[PdX_4]$ (X = Cl, Br) affords dihalopalladium(II) complexes exhibiting *N,O*-ligation of the ligand [77]. Treatment of the phosphohydrazide ligand (**67**) with $[PdCl_2(NCPh)_2]$ gives a metallocycle complex with *N,S*-coordination (**68**). The ligand (**67**) undergoes Schiff's base reactions with, for example, salicylaldehyde to give, after reaction with palladium(II) salts, complexes exhibiting *N,S,O*-coordination (**69**) [78].

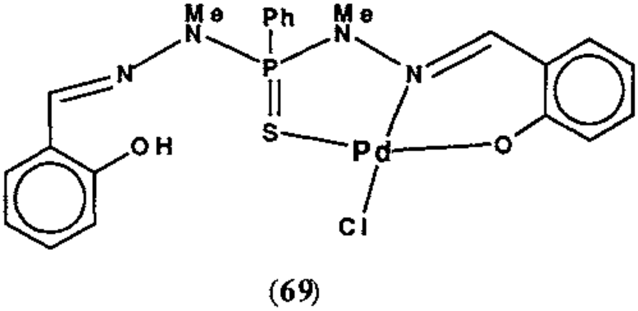
Palladium(II) complexes $[Pd(N,Te)(ClO_4)_2]$, $[Pd(N,Te)_2][ClO_4]_2$ and $[PdCl_2(N,Te)]$ displaying *N,Te*-chelation have been reported for the mixed donor ligand 1-(NMe_2)-2-(TeC_6H_4OEt)-4-MeC_6H_3 [79].



(67)



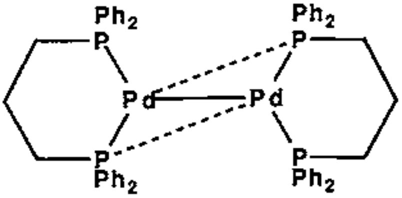
(68)



(69)

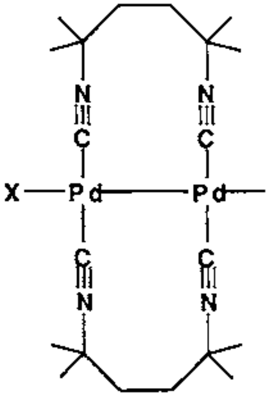
9.3 PALLADIUM(I)

The palladium(II) complex $[Pd(dppp)(CF_3SO_3)_2]$ when treated with H_2 affords the palladium(I) dimer $[Pd(dppp)]_2(SO_3CF_3)_2$. A single crystal *X*-ray diffraction study revealed one phosphorus atom of each dppp ligand occupies an asymmetrically bridging position (**70**), which is removed upon reaction with donor ligands (CO, MeCN) [80].



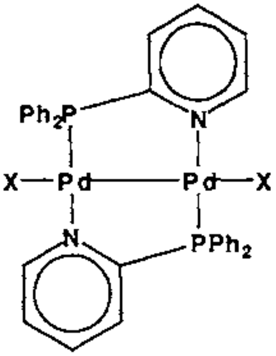
(70)

The phosphido-bridged palladium(I) dimer $[Pd(P^tBu_2H)(\mu\text{-}P^tBu_2)]_2$ has been prepared by UV-irradiation of $Pd(P^tBu_3)_2$ in *n*-hexane or thf, or by reaction of $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ with P^tBu_2H in toluene. The structure of $[Pd(P^tBu_2H)(\mu\text{-}P^tBu_2)]_2$ has also been determined [81]. The reaction of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) with $[Pd_2(diiso)_2X_4]$ (diiso = 1,8-diisocyano-*p*-menthane and 2,5-dimethyl-2,5-diisocyanohexane; X = Cl, Br) affords the dimeric palladium(I) complexes $[Pd_2(diiso)_2X_2]$, *eg*. (71). The complexes have been characterised by IR, NMR and UV-visible spectroscopy and by FAB-mass spectrometry [82].



(71)

The *P,N*-mixed donor ligands $(2\text{-}C_5H_4N)PR_2$ (R = Me, Ph) have been used to prepare a range of palladium(I)-palladium(I) (*eg*. **72**) and palladium(I)-platinum(I) dimers, in which the ligand bridges the two metal centres. The synthetic route involved reaction of the palladium(II) complexes $[PdX_2\{(py)PR_2\}]$ (py = 2-pyridyl) with $[M_2(dba)_3]$ (M = Pd, Pt) [83,84]. Single crystal *X*-ray diffraction structures were reported for the complexes $[MM'Cl_2\{\mu\text{-}(py)PMe_2\}_2]$ (M,M' = Pd_2; Pd, Pt) and $[Pd_2Cl_2\{\mu\text{-}(py)PPh_2\}_2]$ [85].



(72)

9.4 PALLADIUM(0)

The didentate phosphines $R_2PC_2H_4PR_2$ (R = ^iPr, ^tBu) when treated with $[Pd(\eta^3\text{-}C_3H_5)_2]$ in 1,5-hexadiene afford the palladium(0) complexes $[Pd(R_2PC_2H_4PR_2)(\eta^2\text{-}C_6H_{10})]$. In contrast, reaction in pentane (R = ^iPr) or thf (R = ^tBu) yields the dinuclear diastereoisomers rac/meso-$[\{Pd(R_2PC_2H_4PR_2)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_{10})]$ which are converted to the mononuclear species above on treatment with 1,5-hexadiene. In similar reactions, diphosphine-palladium(0) complexes containing η^2-bound 1,5-cyclooctadiene, ethene and ethyne were also prepared [86].

A convenient synthetic route for the production of palladium(0)-phosphine complexes has been reported [87]. The procedure involves reduction of palladium(II)-phosphine complexes using fluoride, and has been investigated for a variety of phosphine ligands and fluoride sources. For example:

$$[PdCl(PPh_3)_3](BF_4) \quad + \quad 2.5\ Bu_4NF{\cdot}3H_2O \quad \rightarrow \quad [Pd(PPh_3)_2]$$

The water soluble complex $[Pd\{P(CH_2OH)_3\}_4]$ has been prepared by treating $[Pd(PPh_3)_4]$ with $P(CH_2OH)_3$. The tetrahedral structure of $[Pd\{P(CH_2OH)_3\}_4]$ has been determined from an *X*-ray diffraction study [88]. Evidence for the formation of the zerovalent palladium complex $[Pd(PPh_3)_4]$ from $[Pd(OAc)_2]_3$ and PPh_3, a common catalyst mixture, has been presented [89]. The Raman spectrum of $[Pd(PPh_3)_2C_{60}]$ has been measured, and the shift to lower frequency of the high frequency C_{60} modes has been proposed to arise from metal → C_{60} π-backbonding [90].

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