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COORDINATION CHEMISTRY REVIEWS

11. Palladium 1993

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CONTENTS

INTRODUCTION

The coordination chemistry of palladium reported during the year 1993 has been reviewed. Although this account does not intend or claim to be comprehensive, examples have been selected to represent important features. Only the primary journals are covered and were searched 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; mixed donor didentate ligands are treated separately.

11.1 PALLADIUM(IV)

The new palladium(IV) complex (**1**) has been prepared by oxidative addition of *p*-nitrobenzyl bromide to the corresponding parent di-organo species. In solution, benzyl group migration to the *aromatic* site slowly occurs with complete regioselectivity, and with a concomitant decrease in the palladium oxidation state [1].

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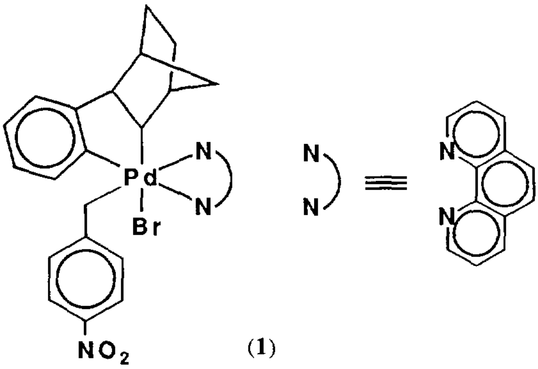
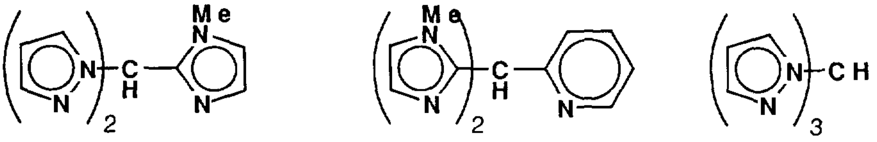


(1)

Palladium(IV) complexes containing ligands such as those displayed in (**2**) have been subjected to Electrospray Mass Spectrometry. In the majority of cases, the intact ion was observed as the base peak at low ion source energies. At higher source energies the palladium(IV) compounds all underwent facile reductive elimination of two methyl groups, as expected [2].



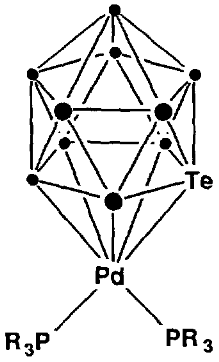
(**2**)

11.2 PALLADIUM(II)

11.2.1 Complexes with phosphine donor ligands

Reaction of $[PdX_2(PR_3)_2]$ (X = Cl, I; PR_3 = PPh_3, $PMePh_2$, PMe_2Ph) with the *nido*-[7-$EB_{10}H_{11}$] (E=Se, Te) anions has been reported [3]. In thf at ambient temperature twelve vertex [2,2-$(PR_3)_2$-*closo*-2,1-$PdEB_{10}H_{10}$] (**3**) is obtained, whilst in refluxing toluene reaction produces only [2-X-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] (**4**). Further reaction of (**4**) (X = I) with Hg^{II} salts affords [2-X-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] (X = Cl, Br, CN, SCN or O_2CMe) complexes (**4**). The solid state structure of (**3**; PR_3 = PMe_2Ph) and (**4**; X = O_2CMe) were determined using X-ray diffraction methods [4]. Further, (**4**; X = I) when treated with $AgBF_4$ in toluene gave [2-(H_2O)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$][BF_4] (**5**), whose solid state structure has been determined by single crystal X-ray diffraction. The H_2O molecule of (**5**) can be replaced by a variety of ligands to produce cationic complexes [2-L-2-(PR_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$][BF_4] (L = *e.g.* CO, $CNBu^t$, NCMe, OC_4H_8, SC_4H_8) (**5**). In the case of (**5**; L = CO) the solid state structure of the molecule has been determined by X-ray crystallography [4].

In a related report, $[PdCl_2(PMe_2Ph)_2]$ reacted with the *nido*-$[7,8\text{-}E_2B_9H_9]^{2-}$ (E = As, Sb) dianions to produce the bis(phosphine)palladium diheteroboranes (**6**). Crystals of the complexes (**6**) were obtained, and their solid structures subsequently determined by X-ray diffraction studies [5].



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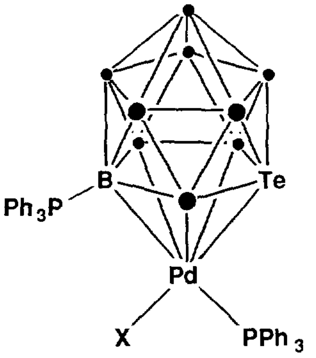

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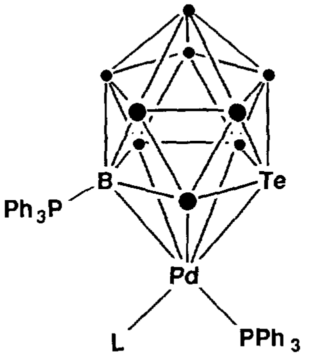
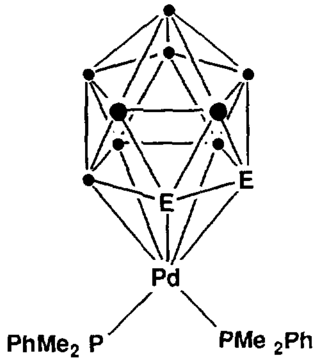


$(5)^+$

• = B-H

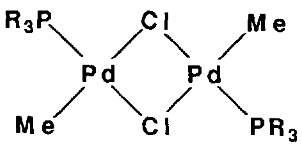


• = B-H

E = As, Sb

(6)

The preparation of $[Pd(\mu\text{-}Br)_2R_4][NBu_4]_2$ and $[PdR_2(NCMe)_2]$ (R = p-$MeC_6H_4SO_2CH_2$) has been reported, and these complexes have subsequently been used to prepare a series of derivatives of general formula $[PdBrR_2L][NBu_4]$ and $[PdR_2L_2]$ (L = *e.g.* PR_3, 4-Mepy) [7]. A convenient procedure for the synthesis of the dinuclear methylpalladium(II) complexes $[Pd_2Me_2(\mu\text{-}Cl)(PR_3)_2]$ (PR_3 = PEt_3, PBu_3, PMe_2Ph, $PMePh_2$ and PPh_3) (7) has appeared. The method involves reaction of $[PdCl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $SnMe_4$ in benzene at room temperature. The dimers (7) react with pyrazoles in the presence of base to give the pyrazolato-bridged compounds (8). Both (7) and (8) adopt a *trans*-configuration [7].



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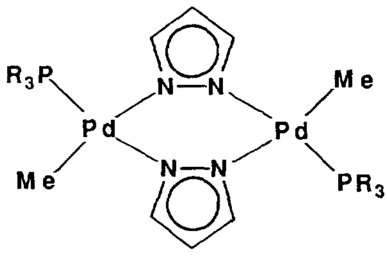
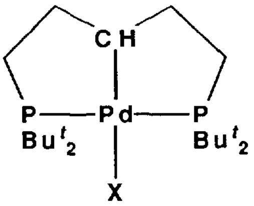


(8)

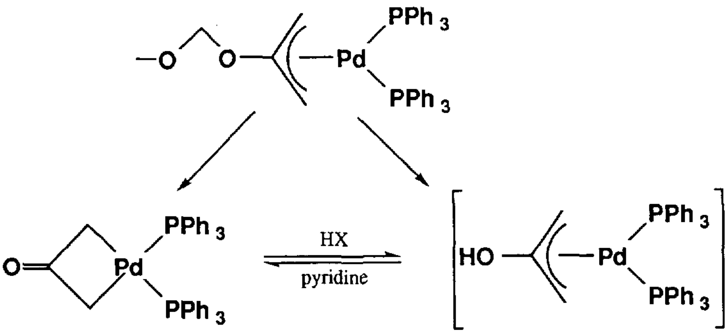
Thermolysis of the dimer $[Pd_2Cl_2\{\mu\text{-}{}^tBu_2P(CH_2)_5P^tBu_2\}_2]$ readily affords the complex (**9**; X = Cl) containing the *P,C,P'*-tridentate ligand (L). Metathesis of this complex with MeLi or $LiAlH_4$ produces the analogous methyl and hydride complexes (**9**; X = H, Me), and complex (**9**; X = Me) can be selectively protonated with $[HNMe_3][BF_4]$ to yield $[Pd(BF_4)L]$; the BF_4 ligand in the complex is readily displaced by coordinating solvents. The solid state structures of [PdMe(L)] and $[Pd(H_2O)L][BPh_4]$ were determined using X-ray diffraction methods [8].



X = Cl, H, Me

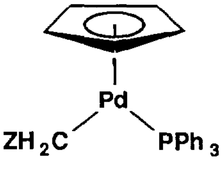
(**9**)

Treatment with base of π-allylpalladium complexes bearing a methoxymethoxy group at the 2-position has been reported to give the corresponding oxodimethylenemethane complex (**10**) in contrast to the formation of 2-hydroxy-substituted π-alkyl complexes (**11**) *via* acidic hydrolysis [9].



(**10**) (**11**)

A series of cyclopentadienyl complexes of the type $[Pd(\eta^5\text{-}C_5H_5)(CH_2Z)(PPh_3)]$ (Z = COPh, COMe, $COCH_2Cl$, CN, SMe) (**12**) have been prepared and characterised. The complexes all react with dry HCl to give $[Pd(\eta^5\text{-}C_5H_5)Cl(PPh_3)]$ as an intermediate, and finally dimeric $[PdCl_2(PPh_3)]_2$ [10]. The palladium triflate complexes $[Pd(OTF)_2(P\text{-}P)]$ (P-P = dppm, dppe, dppp) react with $Tl(C_5H_5)$ to produce the cationic complexes (**13**); the solid state structure of (**13**; P-P = dppe) was determined using X-ray diffraction methods [11]. Cyclopentadienylpalladium(II) complexes have also been obtained by *direct* reaction of cyclopentadiene or methylcyclopentadiene with $[Pd_2Ph_2(\mu\text{-}OH)_2L_2]$ (L = PPh_3, PCy_3). The complex (**14**; L = PPh_3) was structurally characterised by single crystal X-ray diffraction [12].



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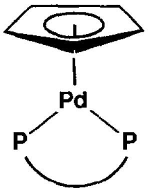

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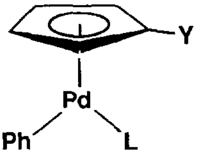
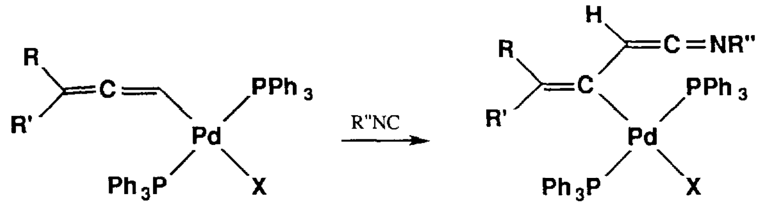


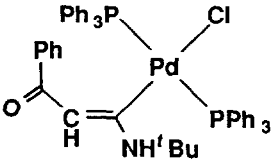
(14)

The *first* square planar *cis*-alkyl(carbonyl) transition metal complex containing a chelating diphosphine has been reported. The complex, $[Pd(Me)(CO)\{(S,S)\text{-BDPP}\}][BF_4]$ $\{(S,S)$-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane$\}$ was prepared by halide abstraction from $[PdMeCl\{(S,S)\text{-BDPP}\}]$ in the presence of CO, and was identified using high pressure NMR spectroscopy [13]. The insertion of isocyanides into the M-C bond of (σ-allenyl)palladium(II) complexes (**15**) has been described. When the R groups on the allenyl ligand are small, insertion affords new (metallovinyl)ketenimine compounds *trans*-$[PdX\{C(CRR')(CH{=}C{=}NR'')\}(PPh_3)_2]$ (**16**) [14].



(15) (16)

The complex $[Pd(CH_2COPh)(Cl)(PPh_3)_2]$ has been prepared by oxidative addition of $PhCOCH_2Cl$ to $[Pd(PPh_3)_4]$, and X-ray analysis has revealed the enolate to be *C*-bonded to palladium. The complex inserts a ^tBuNC molecule into the Pd-C bond to form *trans*-$[Pd\{\text{-}C(NH\text{-}{}^tBu){=}CH\text{-}C(O)Ph\}Cl(PPh_3)_2]$ (**17**), and reacts with $Ag[CF_3SO_3]$ in acetonitrile to give the dimer *cis*-$[Pd_2(\mu\text{-}CH_2COPh)_2(PPh_3)_4]{\cdot}2[CF_3SO_3]$ (**18**). The solid state structure of both (**17**) and (**18**) were obtained using crystallographic methods [15].



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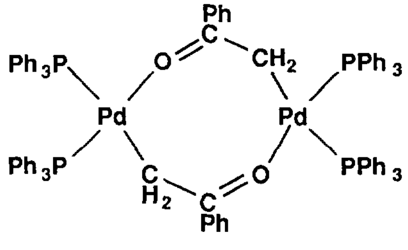
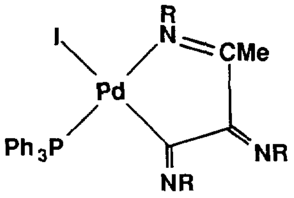
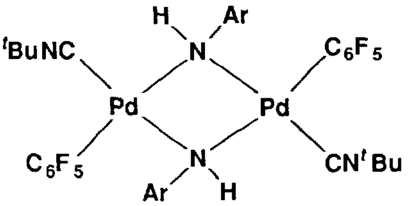


(18)

Treatment of the compounds [Pd(Ar)I(PPh$_3$)$_2$] (Ar = Ph, *p*-MeO-Ph, *p*-Me-Ph, *m*-MeO-Ph) with excess norbornadiene, or reaction of [Pd(PPh$_3$)$_4$] with ArI and norbornadiene has been reported to give the complexes [Pd(C$_7$H$_8$Ar)I(PPh$_3$)$_2$] [16]. Reaction of *trans*-[Pd(Me)I(PPh$_3$)$_2$] with 2,6-xylyl isocyanide in a 1:1 molar ratio led to a spontaneous insertion of isocyanides to give the tris-imino product (**19**) which was structurally characterised by X-ray crystallography [17].



(**19**)

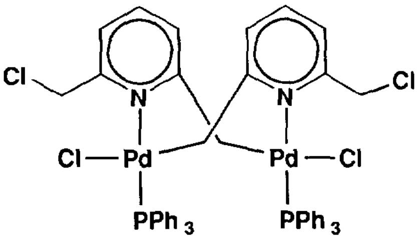


Ar = *p*-C$_6$H$_4$X
X=H, Me, MeO, Cl$^-$, Br$^-$

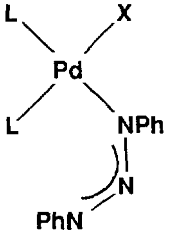
(**20**)

Two series of dinuclear μ-amido palladium(II) complexes of the form [{Pd(C$_6$F$_5$)(PPh$_3$)}$_2$(μ-OH)(μ-NHC$_6$H$_4$X-*p*)] and [{Pd(C$_6$F$_5$)(^{t}BuNC)(μ-NHC$_6$H$_4$X-*p*)}$_2$] (**20**) have been prepared. The solid state structure of (**20**; X = H) has been established using X-ray diffraction [18].

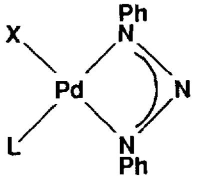
Reaction of [Pd(PPh$_3$)$_4$] with 2,6-bis(chloromethyl)pyridine in toluene at 100°C afforded two oxidative addition products: C^{α},*N*-bridging dinuclear (**21**) and C^{α},*N*,$C^{\alpha'}$-bridging tetranuclear palladium(II) compounds [19].



(**21**)



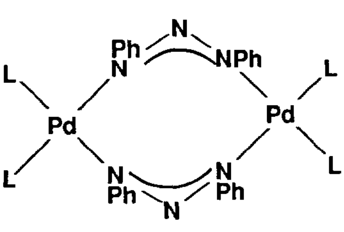
(**22**)



(**23**)

The reaction of [PdX$_2$L$_2$] (X = Cl, Br, mesityl; L = PEt$_3$, PMe$_2$Ph, PPh$_3$, PEt$_3$) with LiPhN(Y)NPh {Y = N, C(Ph)} has been studied. For Y = N, the triazendio ligand forms monodentate (**22**), didentate (**23**) and bridging (**24**) complexes, whilst for Y = C(Ph) complexes containing the bridging amidino group (**25**) were obtained [20].

Resolution of the chiral didentate bis(phosphine) ligand (**26**) has been achieved by fractional crystallisation of a pair of diastereomeric palladium(II) complexes containing the racemic ligand and an orthometallated (*S*)-dimethyl(1-phenylethyl)amine (**27**). The absolute configuration of the (*S*)-enantiomer of the ligand was assigned by a X-ray crystal structure determination of (*R*,*S*)-(**27**) [21].



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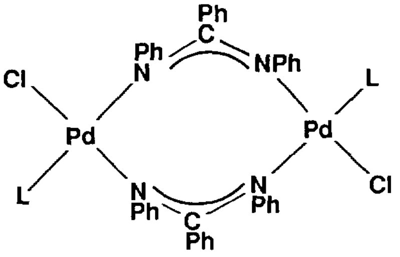

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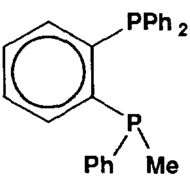
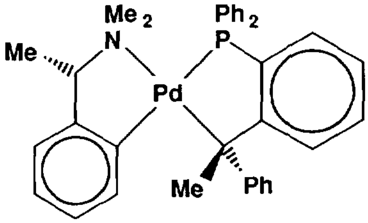
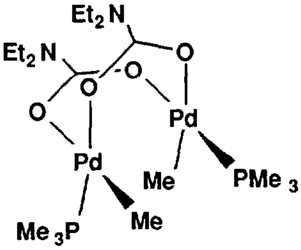


±(26)



(*R*,*S*)-(27)

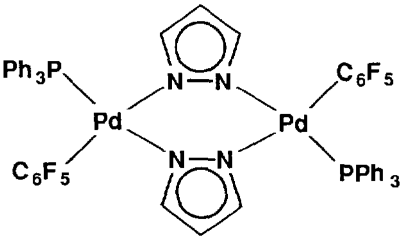
A series of *trans*- and *cis*-methylpalladium carbamate complexes $[PdMe(OCONRR')L_2]$ (L = tertiary phosphine; R, R' = H, alkyl, phenyl) have been reported. The complexes were prepared from the corresponding dimethylpalladium(II) complexes, a primary or secondary amine and CO_2. The dimethylpalladium species also reacted with alcohols and CO_2 to afford alkyl carbonate compounds *trans*-$[PdMe(OCOOR)L_2]$ (R = Me, ^{s}Bu; L = PMe_3, PPh_3). The solid state structure of the dimeric complex $[Pd_2Me_2(\mu\text{-}OCONEt_2)_2(PMe_3)_2]$ (**28**) was determined by X-ray crystallography [22].



(28)

Treatment of $[PdCl_2(dppe)]$ with PhSH in the presence of Bu_3N, or oxidative addition of Ph_2Se_2 to $[Pd(C_2H_4)(dppe)]$ gave the complexes $[Pd(EPh)_2(dppe)]$ (E = S, Se) [23]. In a similar report, complexes of the general formula *cis*-$[M(SC_6F_5)_2L_2]$ (L_2 = dppm, dppe, $2PPh_3$) were synthesised from *cis*-$[MCl_2L_2]$ and $Tl(SC_6F_5)$ [24].

The μ-hydroxo-complexes $[\{PdR(PPh_3)(\mu\text{-}OH)\}_2]$ (R = C_6F_5, C_6Cl_5) have been prepared from reaction of NBu_4OH with the corresponding μ-chloro compounds. Reaction of the hydroxo bridged species with pyrazole or 3,5-dimethylpyrazole afforded the new compounds (**29**) and (**30**), whilst reaction with oxalic (H_2Ox) and acetic (HOAc) acids gave dinuclear [{$PdR(PPh_3)$}$_2$(μ-Ox)] and [{$Pd(C_6F_5)(PPh_3)$(μ-OAc)}$_2$] [25].



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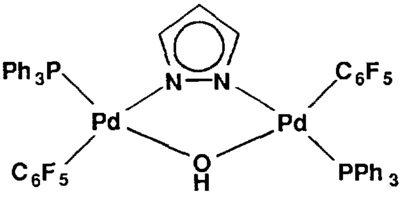
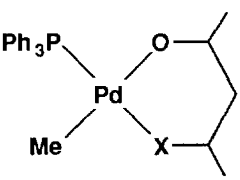


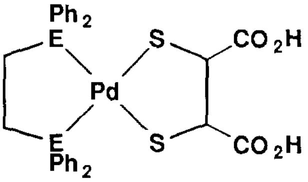
(30)

The solid states of the complexes [PdMe(β-dik)(PPh_3)] (β-dik = acetylacetonate or monothioacetylacetonate) (**31**) have been determined by single crystal X-ray diffraction [26], and the new compounds [Pd(H_2-dmsucc-*S*,*S*')(L-L)] (L-L = dppe, 1-diphenylarsino-2-diphenylphosphinoethane) (**32**) have been reported [27].

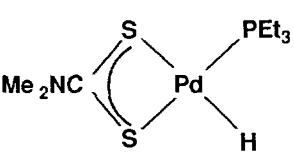
Reaction of [Pd(Me_2NCS_2)(Cl)(PEt_3)] with $LiHBEt_3$ at low temperature affords *in situ* the unstable hydrido species [Pd(H)(Me_2NCS_2)(PEt_3)] (**33**). This species readily inserts alkenes and alkynes into the Pd-H bond, *e.g.* reaction with CH_2=CHCN gives [Pd{CH(CN)CH_3}-(Me_2NCS_2)(PEt_3)] [28]. In a related report, preparation of the hydride complexes *trans*-[PdH(X)$(PPh_3)_2$] (X = Cl, Br) from hydrogenolysis of *trans*-[PdX(COPh)$(PPh_3)_2$] was described [29].



(31) X = O, S



(32) E = P, As



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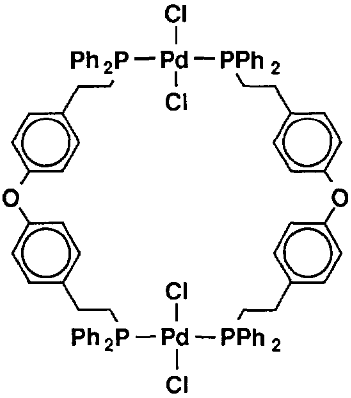
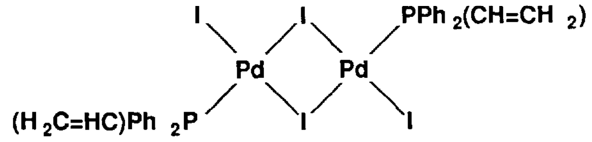


(34)

Treatment of the diphosphine ligand bis[4-{2-(diphenylphosphino)ethyl}phenyl]ether with $Na_2[PdCl_4]$ gave the macrocyclic compound (**34**), apparently from a spontaneous self assembly process [30]. Reaction of the anions $[Ph_2P(Y)PPh_2]^-$ (Y = CH, N) with $[PdX_2L_2]$ (X = Cl, Br; L = PPh_3, PMe_2Ph, PEt_3) complexes has been reported to give a variety of products. Thus, with Y = CH derivatives $[PdCl(Ph_2PCHPPh_2)L]$ were obtained, whilst with Y = N, $[PdX(Ph_2PNPPh_2)(PEt_3)]$ and $[Pd(Ph_2PNPPh_2)_2]$ were isolated. Subsequent treatment of these complexes with HBF_4 yielded the corresponding cationic complexes containing the neutral ligand $Ph_2P(YH)PPh_2$ [31]. The potentially tridentate ligand $HC(PPh_2)_3$ coordinates to palladium(II) *via* two of its PPh_2 sites to afford complexes of the form $[PdXX'\{\eta^2\text{-}(PPh_2)_3CH\}]$ (X = X' = Cl, Br, C_6F_5: X = Cl, X' = C_6F_5) [32].

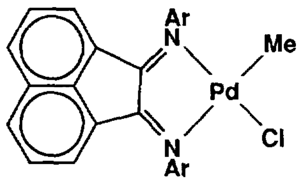


(35)

The unexpected product (**35**) was obtained upon oxidative addition of I_2 to the palladium(I) complex $[(Ph_2PCH_2CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH_2CH_2)Pd]_2[BF_4]_2$, and its solid state structure was established by X-ray crystallography [33]. The mechanism of oxidative addition of arylhalides to low-ligated palladium(0) species, Pd^0L_2 (L = *e.g.* PPh_3), formed by reduction of their divalent precursors has been reported [34].

11.2.2 Complexes with nitrogen donor ligands

Rapid successive, stoichiometric insertions of CO and norbornadiene (R'CH=CHR") into the Pd-C bonds of [PdMeClL] (**36**) leading to stable products of the type [PdC(O)CH(R')CH(R")-C(O)Me] (**37**) have been reported [35]. In a similar report, insertion of CO and norbornene into the Pd-C bond of [Pd{C(O)Me}I(bpy)] has been described [36].



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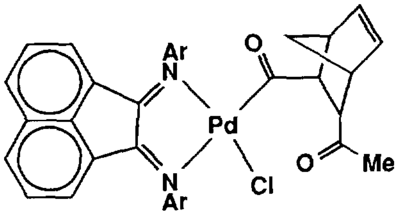
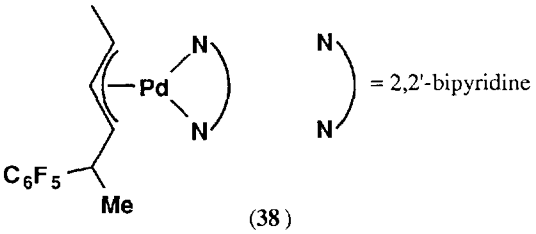


(37)

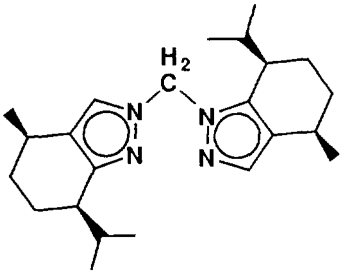
Reaction of $[PdCl_2(bpy)]$ with LiOMe under a CO atmosphere gave the bis(carbomethoxy) compound $[Pd(CO_2Me)_2(bpy)]$. Evidence for the apparent precursor to this complex, i.e. $[Pd(OMe)_2(bpy)]$, was obtained in situ by NMR spectroscopy [37]. The reactivity of *cis*- and *trans*-$[Pd(C_6F_5)(L_2)]^+$ complexes towards dienes has been reported. The *cis*-complex $[Pd(C_6F_5)(bpy)]^+$

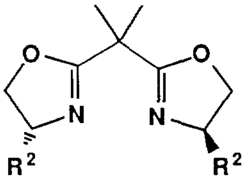
reacts with dienes to afford (C_6F_5-allyl)palladium derivatives, *e.g.* (**38**). However, *trans*-$[Pd(C_6F_5)L_2]^+$, under similar conditions, failed to give analogous products [38].



(38)

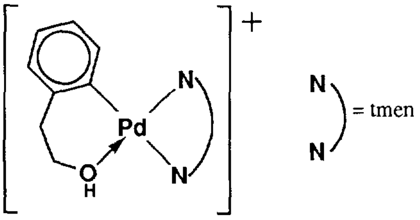
A series of (η^3-C_3H_5)palladium(II) complexes, $[Pd(\eta^3\text{-}C_3H_5)(L_2)][PF_6]$, containing didentate, bis(chiral-pyrazolyl) ligands, *e.g.* (**39**), have been prepared [39]. In a related article, a second series of (η^3-allyl)palladium(II) complexes containing chiral, bis-(oxazoline) ligands, *e.g.* (**40**), were investigated using ^1H NMR spectroscopy [40]. Reaction of (η^3-allyl)palladium chloride dimers with di-2-pyridylsulfide (dps) afforded the series of ionic compounds $[Pd(\eta^3\text{-allyl})(dps)][Pd(\eta^3\text{-allyl})Cl_2]$ in which the dps ligand adopted an *N*,*N*′-binding mode. The solid state structure of the complex with allyl = 2-propenyl was determined using single crystal X-ray diffraction [41].





(39) (40)

Oxidative addition of 2-(2-bromophenyl)ethanol to $[Pd(dba)_2]$ in the presence of tmen afforded the arylpalladium(II) complex $[PdBr\{C_6H_4(CH_2CH_2OH)\text{-}2\}(tmen)]$, which was the subject of an X-ray diffraction study. Halide abstraction using $AgNO_3$ gave the ionic complex $[Pd\{C_6H_4(CH_2CH_2OH)\text{-}2\}(tmen)]NO_3$ (**41**), which was deprotonated using KOMe to yield $[Pd\{C_6H_4(CH_2CH_2O)\}(tmen)]$ [42].



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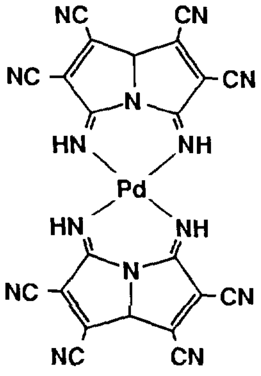

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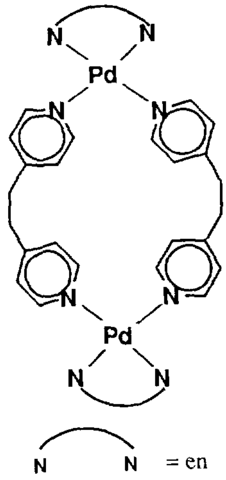
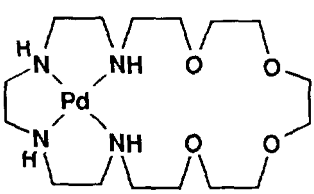


(43)

The neutral, planar complex [PdL_2] (**42**) has been described, along with the crystal structure of its 1,2-dimethoxyethane adduct [43]. Treatment of 1,2-bis(4-pyridyl)ethane with [Pd(en)][NO_3]$_2$ in a 1:1 molar ratio gave the macrocyclic, dipalladium complex (**43**), the structure of which was confirmed by X-ray crystallography [44].

The formation of palladium(II) complexes of [18]aneN_6, [21]aneN_7 and [24]aneN_8 has been studied by microcalorimetry and ^1H and ^{13}C NMR spectroscopy. Crystals of the dinuclear Pd^{2+} complex of [24]aneN_8 were obtained, and were the subject of an Xray diffraction study [45]. The synthesis and structural characterisation of [PdL][PF_6]$_2$ containing cation (**44**) has been reported [46]. The preparation of (terpyridine)palladium(II) complexes of phenylcyanamide anion ligands, *e.g.* (**45**), has been reported, and for (**45**) the solid state structure has been determined by X-ray crystallography [47].



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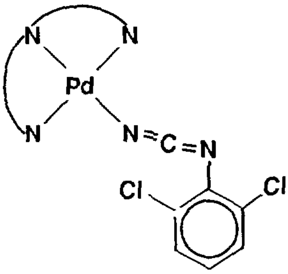
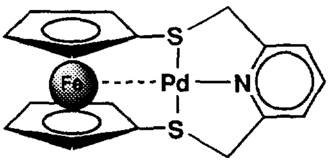


(45)

The palladium(II) complex (**46**) has been reported. The NMR spectral data indicated that the complex possessed a weak Pd----Fe dative bond, and this was supported by an X-ray analysis of the complex [48].



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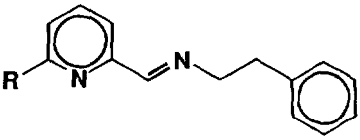
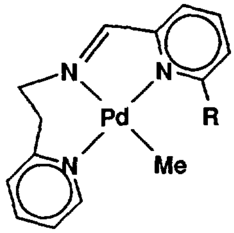


(47) R=H, Me



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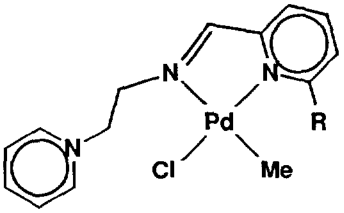
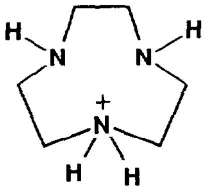


(48)

Treatment of [PdMe(Cl)(cod)] with the ligands (**47**) afforded compounds of the type [PdMe(Cl)(*N*,*N*′-**47**)]$^+$, *e.g.* (**48**), while ionic compounds of the form [PdMe(*N*,*N*′,*N*″-**47**)]$^+$, *e.g.* (**49**), were obtained by halide abstraction of the chlorides using silver(I) salts [49].

The tridentate and didentate coordination behaviour of *N*-(2-hydroxyethyl)-1,2-ethanediamine, L, with PdX_2 (X = Cl, Br), and their *N*,*N*′,*O* to *N*,*N*′ isomerisation behaviour, has been studied using a variety of techniques. One of the isomers, [$PdCl_2$(L)], has been characterised by single crystal X-ray analysis where the palladium was shown to possess the N_2Cl_2 donor set [50]. The synthesis and solid state structures of [$PdCl_2$(L)] and the palladium(II) dimer [(L)Cl_2Pd-$PdCl_2$(L)]$^{2+}$ (L = H[9]aneN_3; **50**) have been reported [51].



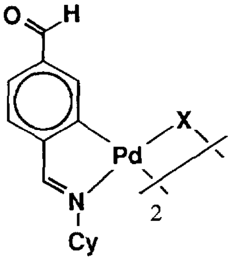
(50)

11.2.3 Cyclometallation complexes

The first examples of optically active, cyclopalladated primary amines were reported. Thus, reaction of [$PdCl_2${$NH_2CH(Me)Ph$}$_2$] with $AgClO_4$, followed by addition of neutral ligands (L_2 =

2py, cod, bpy) or NaBr led to the isolation of [Pd{C_6H_4[CH(Me)NH_2-2]}(L_2)]ClO_4 or [{Pd{C_6H_4[CH(Me)NH_2-2]}(μ-Br)}$_2$] respectively. Some of the complexes were obtained optically pure by employing (*R*)-(+)- or (*S*)-(–)-α-methylbenzylamine as the starting material [52]. In a separate report, the first orthopalladation of unsubstituted benzylamine was described [53].

Treatment of *N*,*N*-terephthalylidenebis(cyclohexylamine) {1,4-$(CyN{=}CH)_2C_6H_4$} with $[Pd(OAc)_2]_3$ gave the monocyclopalladated dimer (**51**), possessing a free formyl group on each phenyl ring. Complex (**51**; X = O_2CMe) was reacted with halide ions to form (**51**; X = Cl, Br, I), and (**51**; X = Cl, Br, I) with Tl(acac) to give (**52**), or with tertiary phosphines to give (**53**) [54].



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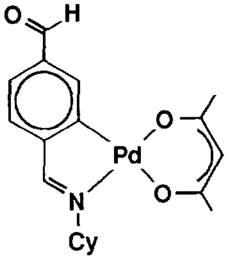

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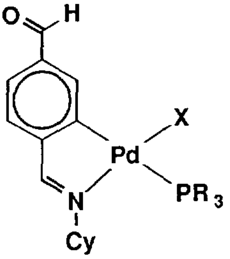
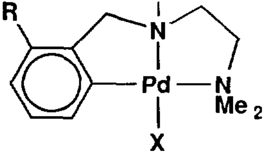


(53)

Cyclometallation of *N*-benzyl and *N*-(phenylethyl)-α-benzoylbenzylideneamines with $[Pd(OAc)_2]_3$ has been investigated. A five membered endo-metallocycle involving the less activated aromatic ring is formed in all cases. The solid state structure of one of the derivatives [Pd{C_6H_4(C_6H_5C=O)C=NCH(Me)C_6H_5}(O=SMe_2)Cl] has been established [55]. The synthesis of new terdentate *C*,*N*,*N*′-bound aryl, benzyl and alkyl organopalladium compounds has been reported, *e.g.* (**54**). By attention to ligand design, palladation can be directed towards sp^2 and sp^3 C-H activation and towards 5-membered or 6-membered ring formation [56].

The reaction of $[Pd(OAc)_2]_3$ and the imines of general formula $C_6R_mH_{5\text{-}m}CH{=}N(CH_2)_pC_6R'_nH_{5\text{-}n}$ has been studied. Five-membered and 6-membered *endo*-macrocycles from C(aromatic)-H and C(aliphatic)-H activation, respectively, were obtained. The account also reported the formation of cyclopalladated complexes formed by oxidative addition of *ortho* C(aromatic)-Cl bonds [57]. The preparation of cyclometallated [PdLCl] (HL = 6-^{t}butyl-2,2′-bipyridine), (**55**), has been described. The deprotonated bipyridine is tridentate through the two N atoms and a carbon of the ^{t}butyl group [58].



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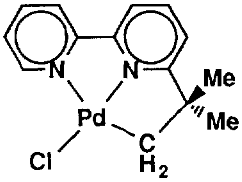

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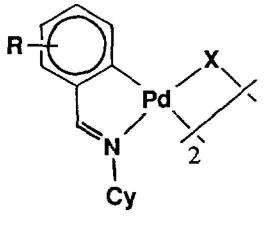

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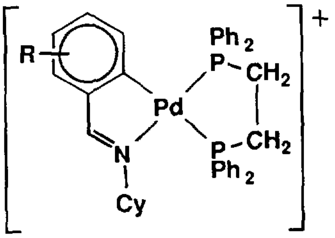

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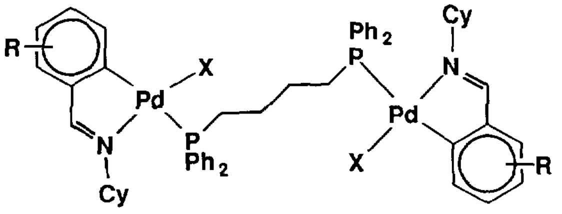
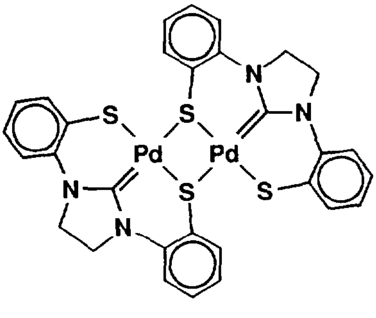


(58)

In two related reports, treatment of Schiff bases {*e.g.* 4-$MeC_6H_4C(H){=}NCy$; 3-Me-4-$MeOC_6H_3C(H){=}N$-2',4',6'-$Me_3C_6H_2$; 2,4-$R_2C_6H_3C(H){=}NCy$ (R=Me, OMe)}, with palladium(II) acetate gave the corresponding cyclometallated acetato-bridged complexes which could be converted into the analogous halo-bridged species upon reaction with NaX, *e.g.* (**56**). These dimers were subsequently reacted with a variety of bis(phosphines) to give mononuclear, *e.g.* (**57**), and dinuclear, *e.g.* (**58**), complexes [59, 60].

11.2.4 Complexes with sulfur donor ligands

Treatment of $K_2[Pd(S_2C_2O_2)_2]$ with 2-methylpyridinium hydrochloride in aqueous solution afforded the compound $(HC_6H_7N)_2[Pd(S_2C_2O_2)_2]$ [61]. The palladium(II) complex $[Pd('S_2C')]_2$ ('S_2C' = 1,3-imidazolidinyl-N,N'-bis(2-benzenethiolate) (**59**) has been prepared in a one pot synthesis from $[PdCl_2(cod)]$, 1,2-ethanediamine-*N*,*N*'-bis(2-benzenethiolate) and $CH(OEt)_3$. Reaction of (**59**) with pyridine gave $[Pd(py)('S_2C')]$ (**60**) [62].



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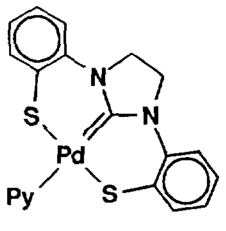

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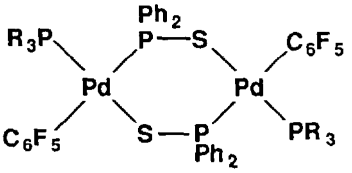
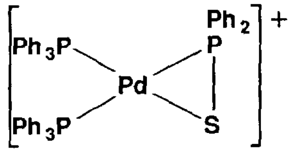
11.2.5 Complexes with mixed donor ligands

The neutral dimer complexes $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PR_3)\}_2]$ (**61**) ($PR_3 = PPh_3, PPh_2Et$) containing the bridging $[SPPh_2]^-$ ligand, and cationic complexes $[Pd(SPPh_2)(PPh_3)_2]^+$ (**62**) containing $[SPPh_2]^-$ as a *P,S*-chelate have been reported. The crystal structures of two of these, $[\{Pd(\mu\text{-}SPPh_2)(C_6F_5)(PPh_3)\}_2]$ and $[Pd(SPPh_2)(PPh_3)_2]ClO_4$, have been established using X-ray diffraction methods [63]. The thioyl and selenoyl compounds $Ph_2PN(Ph)PPh_2{=}E$ (E = S, Se) act as chelating didentate ligands, and form complexes $[PdCl_2(L)]$ containing the Cl_2(P-S) and Cl_2(P-Se) donor set [64]. The synthesis of $[PdCl_2\{\pm Ph_2ECH_2CH_2S(O)Me\}]$ (E = As, P) and the solid state structure of $[PdCl_2\{\pm Ph_2PCH_2CH_2S(O)Me\}]$ have been described [65].

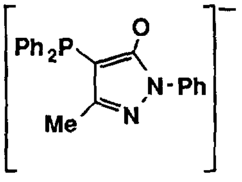


(**61**)

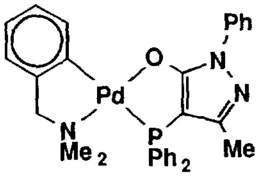


(**62**)

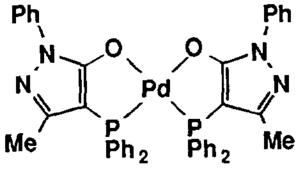
Neutral and cationic allyl-palladium(II) complexes containing the *P,O*-didentate ligands $[Ph_2P(CH_2)_nCO_2]^-$ (n = 1 to 3) or $Ph_2P(CH_2)_nCO_2R$ (n = 1 to 3; R = Me, Et) have been reported. For the neutral allyl-palladium complexes containing the ligands $[Ph_2P(CH_2)_nCO_2]^-$ (n = 1, 2) the solid state structures were established using X-ray diffraction methods [66]. Reaction of the sodium phosphinopyrazolonate (**63**) with $[Pd(o\text{-}C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]_2$ and $[Pd(acac)_2]$ yields the chelate complexes (**64**) and (**65**), respectively. The molecular structure of (**65**) was determined crystallographically [67]. Optical resolution of the asymmetric chelate (±)-$[Ph_2ECH_2\text{-}CH_2S(O)Me]$ (E = As, P) via fractional crystallisation of a pair of diastereomeric palladium(II) complex cations containing ortho-metallated (*S*)-{1-(dimethylamine)ethyl}naphthalene has been reported [68].



(**63**)

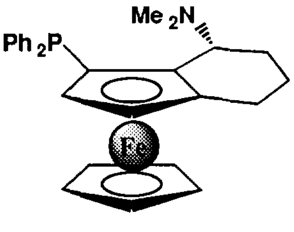


(**64**)



(**65**)

The preparation of a new ferrocenylaminophosphine ligand (**66**) has appeared along with the synthesis and solid state structure of its palladium dichloride complex [69]. The preparation of the valine-derived chiral (L) *P,N*-didentate ligand (**67**) and its $PdCl_2$ complex has been reported [71].



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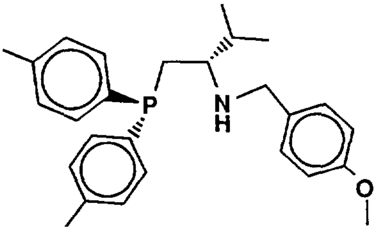

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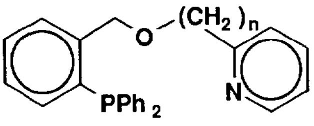
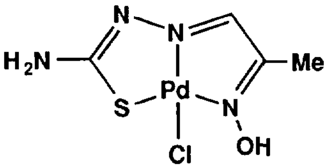


(68)

Treatment of [Pd{η^3-$CH_2C(Me)CH_2$}(Ph_2Ppy)Cl] with *cis*-[Pd($^tBuNC)_2Cl_2$] affords the new compound *cis*-[Pd($^tBuNC)_2(Ph_2Ppy)Cl_2$] in which the potentially didentate *P,N*-donor ligand is monodentate through phosphorus only [71]. A series of new *P,N*-didentate ligands capable of *trans* chelation have been prepared. The ligands *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2 (n = 1 to 3), **(68)**, when treated with Na[$PdCl_4$] or [$PdCl_2(PhCN)_2$] in an equimolar ratio gave mainly the 1:1 complexes [$PdCl_2${*o*-$Ph_2PC_6H_4CH_2O(CH_2)_nC_5H_4N$-2}]. When n = 1, *cis* complexes were formed, but with longer bridges (n = 2, 3) *trans*-complexes were the main products [72].

The solid state structure of the complex [Pd([9]ane$NS_2)_2$][$BF_4]_2$, ([9]aneNS_2 = 1, 4-dithia-7-azacyclononane) has been reported [73]. A series of methionine complexes [PdX_2L]•dmp (X = Cl, Br, I; L = D-, L- or DL-methionine; dmp = 2,6-dimethyl-4H-pyran-4-one) have been prepared by reaction of PdX_2 with methionine in the presence of dmp. The solid state structure of [PdI_2(DL-L)]•dmp was determined using X-ray crystallography [74]. The synthesis and crystal structure of **(69)** has been described [75]. Treatment of [$Pd(PPh_3)_4$] with *trans*-[$PhSNC(MeC_6H_4)N{=}NC(MeC_6H_4)NSPh$] in toluene produces **(70)**, in which the ligand is bonded to palladium in an *N,N′,S*-tridentate fashion [76].



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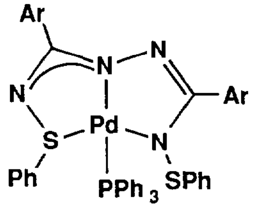
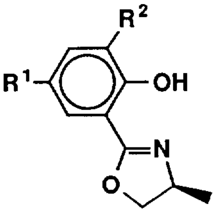
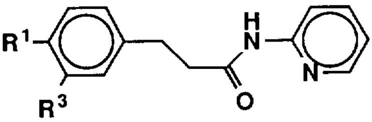


(70) Ar=4-MeC_6H_4

A series of (η^3-allyl)palladium(II) derivatives of chiral *N,O*-didentate ligands **(71)** have been synthesised to assess their potential as model intermediates for regio- and stereo-controlled catalytic allylic alkylation and substitution reactions. Crystals of the complex [Pd(η^3-cyclohexenyl){*N*-(α-methylbenzyl)salicylaldimine}] were obtained as a single isomer and subjected to X-ray crystallography [77]. Reaction of the ligand *N*-(2-pyridyl)-3-phenyl-2-propene amide (N-O) (72) with $PdCl_2$ gave [$PCl_2(N\text{-}O)_2$], in which only the pyridyl nitrogen was coordinated [78].



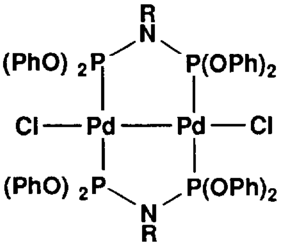
(71)



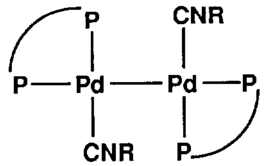
(72)

11.3 PALLADIUM(I)

Redox condensation of [$Pd_2(dba)_3$] with [$PdCl_2(PhCN)_2$] in the presence of $RN[P(OPh)_2]_2$ (R = Me, Ph) gave the dinuclear complexes (73). The structures have been deduced from ^1H and ^{31}P NMR spectroscopy, and confirmed by single crystal X-ray diffraction studies on (73; R = Ph) [79]. Electrolysis of the complexes [Pd(P-P)(RNC)$_2$][PF_6]$_2$ (R = 2,6-Me_2 or 2,4,6-Me_3-phenyl; P-P = dppm, dppe, dppp, dppb) afforded the dinuclear palladium(I) species (74); for (74; R = 2,6-$Me_2H_6H_3$; P-P = dppm) the solid state structure has been determined by X-ray crystallography [80].

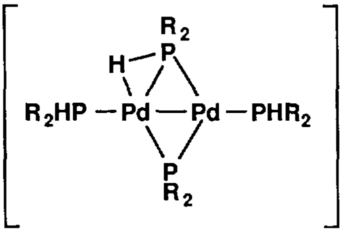


(73)

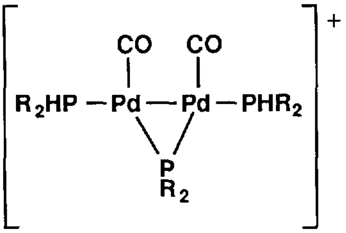


(74)

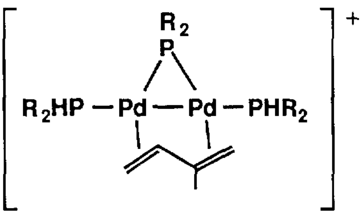
Treatment of the A-frame precursor complexes [$Pd_2X_2(dppm)_2$] (X = Cl, Br, I) with arenediazonium salts [*p*-$YC_6H_4N_2$][BF_4] (Y = H, Me, OMe, F, NO_2) afforded 1:1 adducts containing a symmetrically bridging arenediazenido ligand. The crystal structures of [$Pd_2I_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4Me)$][$BF_4$] and [$Pd_2Cl_2(dppm)_2(\mu\text{-}N_2\text{-}p\text{-}C_6H_4F)$][$BF_4$] were determined [81]. Two unusual cationic palladium(I) dimers containing bridging P^tBu_2 and terminal PH^tBu_2 ligands have been reported. The first of these, (75), contains a Pd-H-P bridging unit, whilst the other, prepared from (75), possesses terminal CO ligands (76). For both complexes the solid state structure was determined crystallographically [82]. In a separate, but related report, (75) reacted with excess isoprene to yield (77), which was characterised using X-ray diffraction and NMR spectroscopy [83].



(75)

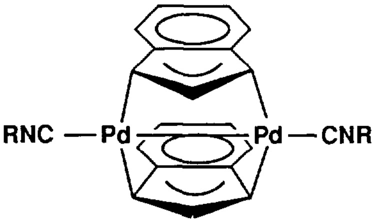


(76)

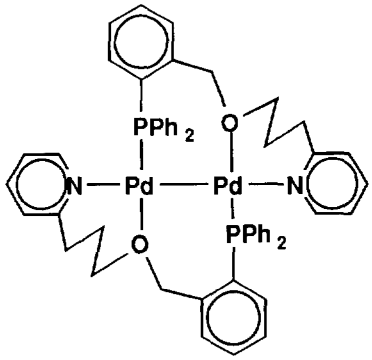


(77) R=^{t}Bu

A series of dinuclear palladium(I) complexes containing a bridging η^3-indenyl ligand have been described. The complexes (78) were prepared from reaction of $[PdCl_2(RNC)_2]$ with lithium indenyl [84]. The preparation and crystallographic structure of a cationic palladium(I) dimer containing a *P,O,N*-tridentate ligand has been reported. The complex, (79), possesses an extremely short Pd----Pd bond [2.500(1) Å] [85].



(78)

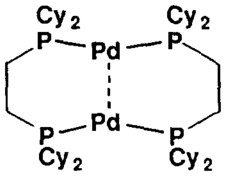


(79)

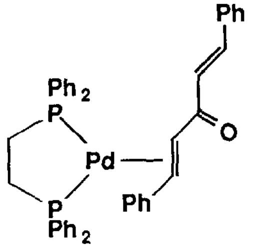
11.4 PALLADIUM(0)

The preparation and single crystal X-ray analysis of [Pd(CO)(triphos)] {triphos = $MeC(CH_2PPh_2)_3$} have been reported [86]. The first palladium(0) complex containing only secondary phosphines as ligands, $[Pd(P^tBu_2H)_3]$, has been prepared by treating $[Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}$

C_5H_5)] with P^tBu_2H [87]. The photolysis (at 254 nm) of the palladium oxalate [Pd(C_2O_4)(dcpe)] afforded, in high yield, the dinuclear palladium(0) complex (**80**). The solid state structure of (**80**) has been determined, and possesses a very short Pd----Pd distance of 2.7611(5) Å [88].



(**80**)



(**81**)

A range of mixed bisphosphine complexes of palladium(0) has been prepared and the complexes have been characterised by ^{31}P NMR spectroscopy [89]. Treatment of [Pd(dba)$_2$] with one equivalent of a chelating phosphine ligand (P-P), or two equivalents of a monodentate phosphine ligand (P) affords complexes of the form [Pd(dba)(P-P)] (**81**). The crystal structure of [Pd(dba)(dppe)] has been established by X-ray diffraction [90]. Buckminsterfullerene, C_{60}, when treated with [Pd(PPh_3)$_4$] gave a high yield of [Pd(C_{60})(PPh_3)$_2$], in which fullerene is ligated in an η^2-fashion, as determined by crystallography [91].

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