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Review

Aqua palladium complexes: synthesis, properties and applications

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Contents

Abbreviations: ampy, 2-NHpyridine; BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; bpy, 2,2′-bipyridine; bquin, benzoquinoline; COD, 1,5-cyclooctadiene; DACH, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane; dien, diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$); dippf, 1,1′-bis(diisopropylphosphino)ferrocene; dmp, 2-(dimethylaminomethyl)phenyl; dppe, 1,2-bis(diphenylphosphino)ethane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dppma, $Ph_2PN(Me)PPh_2$; dppomf, 1,1′-bis(diphenylphosphino)octamethylferrocene; dppp, 1,3-bis(diphenylphosphino)propane; dppr, 1,1′-bis(diphenylphosphino) ruthenocene; dtco, 1,5-dithiacyclooctane; dtcol, 1,5-dithiacyclooctan-3-ol; en, ethylenediamine; Et_4dien, $Et_2N(CH_2)_2NH(CH_2)_2NEt_2$; Fmes, 2,4,6-tris(trifluoromethyl)phenyl; Hgu, guanosine; Hampy, 2-aminopyridine; MeOazb, 2-(4-methoxyphenylazo)phenyl; Mequin, 8-methylquinoline; MetOMe, methionine methyl ester; OAc, acetate; PCy_3, tricyclohexylphosphine; phen, 1,10-phenanthroline; py, pyridine; $(pz)_3BH$, tris(pyrazol-1-yl)borate; TfO^-, trifluoromethanesulfonate ($CF_3SO_3^-$); THF, tetrahydrofuran; thpy, 2-thienylpyridine; tht, tetrahydrothiophene; To, C_6H_4Me-4; TsO, *p*-toluenesulfonate (4-$MeC_6H_4SO_3$)

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Abstract

Contrary to quite general opinion, many aqua palladium complexes have been isolated and characterized. In this review, we present the first comprehensive study of the synthesis of aqua palladium complexes and their properties. The methods of preparation have been classified according to the nature of the starting palladium complexes. The spectroscopic properties (IR, NMR, UV–vis), the kinetic and reaction mechanisms, the theoretical studies and the crystal structures of aqua palladium complexes are studied. Of particular interest are their many applications as catalysts in very different processes. Thus, their uses for the synthesis of other complexes, as artificial metallo-peptidases and -proteases, and other catalytic applications have been reviewed.

Keywords: Aqua; Palladium; Complexes; Hydrogen bonding; Metallo-peptidases; Metallo-proteases

1. Introduction

Aqua palladium complexes are of interest because some are relevant in catalytic processes or as intermediates in reactions carried out in solution. Both characteristics are related with the easy replacement of the hard base H_2O associated with the soft acid Pd(II). This is the reason for the considerable number of known cationic complexes where the metal center will be harder, and the few isolated neutral or anionic aqua palladium(II) complexes reported. Although the harder Pd(IV) is expected to be too acidic to give stable aqua complexes, a few such complexes have been reported. However, as we will discuss latter, they may be considered as intermediate between hydroxo and aqua complexes.

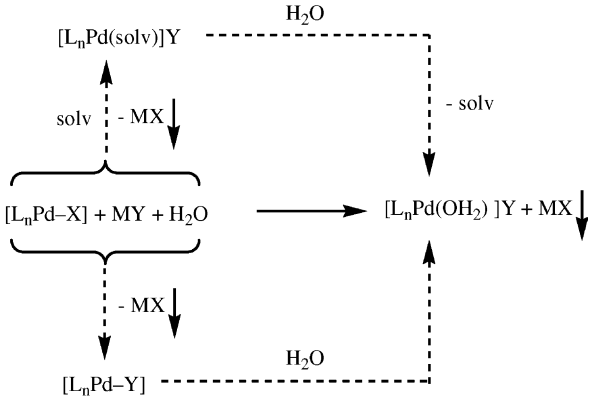
In spite of the great number of aqua complexes and its importance, comprehensive inorganic chemistry collections give a poor view of this field because they only dedicate a short phrase to the $[Pd(OH_2)_4](ClO_4)_2$ complex [1,2] or state that "oxygen-containing solvents such as water, alcohols or ethers are such poor donors that few complexes with palladium(II) have been isolated" [3]. Probably, the use of these old references is the reason why most papers reporting aqua palladium complexes consider them much more rare than actually they are; a few recent papers show a distorted vision of this topic [4–6] or even ignore the precedents [7–9]. Contrary to the quite general opinion of most of the authors mentioned in this review, many aqua palladium complexes have been isolated and characterized (more than a hundred; 53 of which have been studied by X-ray diffraction). In addition, many others have been characterized in solution, although not isolated. However, the proposed formulations or/and structures of a few, prepared 30–40 years ago and characterized by elemental analyses, and some prepared and used in solution without isolation should be taken with caution.

2. Methods of preparation

The purpose of this chapter is to describe the methods of synthesis of aqua palladium complexes that have been isolated. Some of those prepared in solution and/or used without isolation will be discussed later.

2.1. Reactions of halo palladium complexes with salts of weakly coordinating anions

The reactions of halo palladium complexes with silver or thallium or other salts of weakly coordinating anions (e.g., ClO_4^-, BF_4^-, SbF_6^-, BPh_4^-, SO_4^{2-}, TfO^-, TsO^-) in solvents with poor donor abilities (e.g., chlorocarbons), especially when they are not thoroughly anhydrous, or when working in water, facilitate the direct synthesis of aqua palladium complexes. However, in some of these reactions, the synthesis of the aqua complexes proceed through species like $[L_nPd–Y]$ (Y = anion) or a solvento complex $[L_nPd(solv)]Y$, depending on the coordination ability of Y^- or of the solvent competing with water for the acid moiety L_nPd^+ (Scheme 1).



Scheme 1. Different routes to formation of aqua palladium(II) complexes.

Usually, substitution of Y^- or the solvent by H_2O after crystallization gives an aqua complex (often unintentionally) due to atmospheric moisture or the presence of water in the solvents or in the used salt.

The starting compounds for these reactions can be mono- or di-halo palladium complexes.

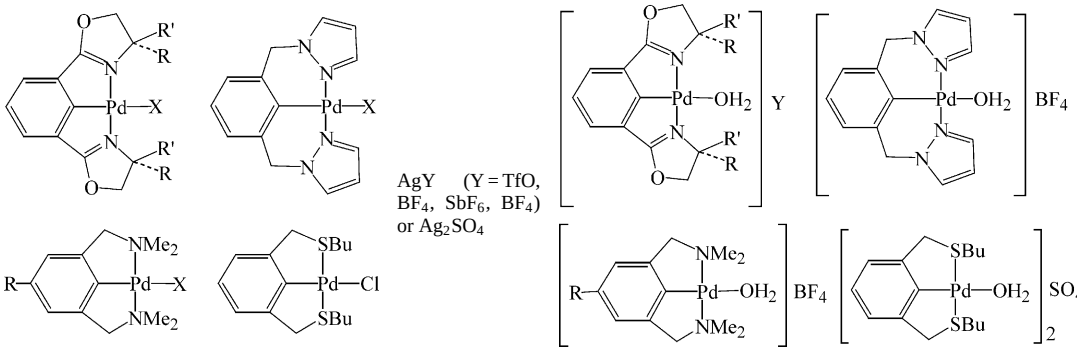
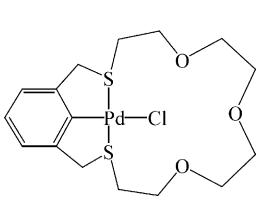
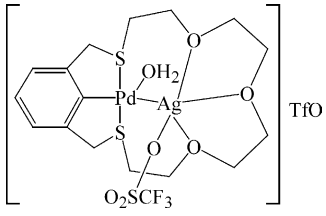
Silver salts are the most usual precipitating reagent. Thus, for example, $AgBF_4$ reacts with [2-I-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] (Table 1, line 1.1) or with a series of chloro or bromo pincer complexes (Table 1, line 1.2) to give [2-(OH_2)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]BF_4 [10] or the corresponding aqua pincer complexes [6,9,11–18], respectively.

$AgClO_4$ in water or in toluene/water reacts with an half equivalent of the complex [PdI(dien)]I (Table 1, line 1.3) to give $[Pd(dien)(OH_2)](ClO_4)_2$ [19,20]. $[Pd_2(dmp)_2(\mu\text{-}Cl)_2]$ does not react with Mequin or bquin but does react with $AgClO_4$ in acetone and, after filtering off the AgCl, addition of the stoichiometric amount of L (Table 1, line 1.4) gives complexes $[Pd(dmp)L(OH_2)]ClO_4$ (L = Mequin, bquin, 2,9-dimethyl-1,10-phenanthroline) [21]. Similarly, the reactions of the palladium complexes containing N^{21},N^{22}-ethene porphyrins $[PdCl_2(N^{21},N^{22}\text{–}C(R)\text{=}C(R)\text{–}X)]$ (R = Ph, X = 5,10,15,20-tetraphenylporphyrin dianion (TPP), 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; R = Et, X = TPP) (Table 1, line 1.5) with $AgClO_4$ give the corresponding cationic diaqua complexes [22].

Ag_2SO_4 (Table 1, line 1.2) [23], AgTfO (Table 1, lines 1.6 and 1.7) [24,25], AgTsO (Table 1, line 1.8) [4], TlTfO (Table 1, line 1.9) [26] and $NaPF_6$ (Table 1, line 1.10) [7] have also been used. Some authors have prepared a series of cationic complexes using different AgX salts: X = TfO, BF_4, SbF_6 (Table 1, line 1.2) [27,28].

Reactions of $[PdCl_2L_2]$ (Table 1, line 1.11) (L = PPh_3 [29], L_2 = dppf [30], dppomf, dppomf(BF_4) [31], BI-

Table 1
Synthesis of aqua palladium complexes from halo palladium complexes and salts of weakly coordinating anions

Line	Starting palladium complex	Precipitating reagent	Aqua palladium complex	Ref.
1.1	[2-I-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]	$AgBF_4$	[2-(OH_2)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]BF_4	[10]
1.2		AgY (Y = TfO, BF_4, SbF_6, BF_4) or Ag_2SO_4		[6,9,11–18,23,27,28]
1.3	[PdI(dien)]I	$AgClO_4$	$[Pd(dien)(OH_2)](ClO_4)_2$	[19,20]
1.4	$[Pd_2(dmp)_2(\mu\text{-}Cl)_2]$	(i) $AgClO_4$; (ii) L[a]	$[Pd(dmp)L(OH_2)]ClO_4$	[21]
1.5	$[PdCl_2(N^{21},N^{22}\text{-}C(R)\text{=}C(R)\text{-}X)]$[b]	$2AgClO_4$	$[Pd(OH_2)_2(N^{21},N^{22}\text{-}C(R)\text{=}C(R)\text{-}X)](ClO_4)_2$	[22]
1.6	[PdCl(Me)(P∼N)][c]	AgTfO	[PdMe(OH_2)(P∼N)]TfO	[24]
1.7		AgTfO		[25]
1.8	*trans*-[Pd(CO_2Me)Cl(PPh_3)$_2$]	AgTsO	*trans*-[Pd(CO_2Me)(OH_2)(PPh_3)$_2$]TsO	[4]
1.9	$[Pd\{C_6H_4C(O)Me\text{-}2\}(\mu\text{-}Br)(PPh_3)]_2$	TlTfO	$[Pd\{C_6H_4C(O)Me\text{-}2\text{-}C,O\}(OH_2)(PPh_3)]TfO$	[26]
1.10	[Pd(Cl(dmp)(PPh_3)]	$NaPF_6$	[Pd(dmp)(OH_2)(PPh_3)]PF_6	[7]
1.11	$[PdCl_2L_2]$[d]	2AgX	*cis*-$[PdL_2(OH_2)_2]X_2$ (X = TfO, BF_4, TsO)	[29–33]
1.12	$[PdCl_2L_2]$[e]	AgTfO in MeCN	$[Pd(NCMe)L_2(OH_2)](TfO)_2$	[34]
1.13	$[PdCl_2\{(S)\text{-MeO-BIPHEP}\}]$[f]	2AgX (X = TfO, BF_4) in THF or acetone	$[Pd\{(S)\text{-MeO-BIPHEP}\}(OH_2)_2]X_2$ (X = TfO, BF_4), $[Pd(OTs)\{(S)\text{-MeO-BIPHEP}\}(OH_2)]TsO$, $[Pd\{(S)\text{-MeO-BIPHEP}\}(OH_2)(THF)](TfO)_2$	[35]
1.14	$[PdCl_2(NCPh)_2]$ + MeOazbH	Excess of $AgClO_4$	$[Pd(MeOazb)(NCPh)(OH_2)]ClO_4$	[36]

[a] L = Mequin, bquin, dmphen.
[b] R = Ph, X = 5,10,15,20-tetraphenylporphyrin dianion (TPP), 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; R = Et, X = TPP.
[c] P∼N = $Ph_2PC_6H_4N$=CHPh-2-*C*,*N*.
[d] L = PPh_3, L_2 = dppf, dppomf, dppomf(BF_4), BINAP.
[e] L_2 = dppf, dppr, dippf, dppp, BINAP.
[f] MeO-BIPHEP = 6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine).

Table 2
Synthesis of aqua palladium complexes by reacting water with palladium complexes containing weakly coordinated anions

Line	Starting palladium complex	Aqua palladium complex	Ref.
2.1	$[Pd(OTf)_2(dppp)]$	$[Pd(OTf)(OH_2)(dppm)]TfO$, $[Pd(OH_2)_2(dppp)](TfO)_2$	[38]
2.2	$[PdR(OClO_3)(tht)_2]$[a]	$[PdR(OH_2)(tht)_2]ClO_4$	[39]
2.3	$[Pd(Ar)(OTf)(PEt_3)]$[b]	$[Pd(Ar)(OH_2)(PEt_3)]TfO$	[40]

[a] R = $C_6H_2(NO_2)_3$-2,4,6.
[b] Ar = C_6H_3N=NTo-2,Me-5-*C*,*N*.

NAP [32,33]) with 2 equiv. of AgX give the corresponding complexes *cis*-$[PdL_2(OH_2)_2]X_2$ (X = TfO [29–31,33], BF_4 [32], TsO [31]). However, when a more coordinating solvent is used, the monoaqua complex can be isolated. Thus, reactions of some of the above complexes $[PdCl_2L_2]$ with 2 equiv. of AgTfO in MeCN (Table 1, line 1.12) lead to the monoaqua complexes $[Pd(NCMe)L_2(OH_2)](TfO)_2$ (L_2 = dppf, dppr, dippf, dppp, BINAP) [34]. The addition of 2 equiv. of AgX (X = TfO, BF_4) in THF or acetone to $[PdCl_2\{(S)$-MeO-BIPHEP$\}]$ (MeO-BIPHEP = 6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine)) (Table 1, line 1.13) leads to the formation of the cationic diaqua $[Pd\{(S)$-MeO-BIPHEP$\}(OH_2)_2]X_2$ (X = TfO, BF_4) and monoaqua complexes $[Pd(OTs)\{(S)$-MeO-BIPHEP$\}(OH_2)]TsO$. Exchange of a water molecule by THF is observed for $[Pd\{(S)$-MeO-BIPHEP$\}(OH_2)_2](TfO)_2$ to yield the monoaqua complex $[Pd\{(S)$-MeO-BIPHEP$\}(OH_2)(THF)](TfO)_2$ [35]. A special case is the synthesis of the monoaqua cyclopalladated complex $[Pd(MeOazb)(NCPh)(OH_2)]ClO_4$ (Table 1, line 1.14), formed when an excess of $AgClO_4$ is added to an equimolar solution of $[PdCl_2(NCPh)_2]$ and 4-methoxyazobenzene (MeOazbH) in THF [36].

2.2. Reactions of water with palladium complexes containing weakly coordinated anions

Sometimes, it is possible to isolate the neutral palladium complexes $[PdY_2L_2]$ obtained following the method given in Section 2.1 and to use them to prepare aqua palladium complexes. Thus, the complex $[Pd(OTf)_2(dppp)]$ prepared from $[PdCl_2(dppp)]$ and AgTfO [37] reacts with 1 or 2 equiv. of water to yield $[Pd(OTf)(OH_2)(dppm)]TfO$ or $[Pd(OH_2)_2(dppp)](TfO)_2$ (Table 2, line 2.1), respectively [38]. We have reported that complex $[Pd(R)Cl(tht)_2]$ (R = $C_6H_2(NO_2)_3$-2,4,6) reacts in acetone with $AgClO_4$ to give the neutral perchlorato complex $[PdR(OClO_3)(tht)_2]$ even though the reaction was carried out without any special precautions to exclude moisture. Only when a precipitating solvent is allowed to diffuse slowly into a solution of $[PdR(OClO_3)(tht)_2]$ in the air, is the aqua complex $[PdR(OH_2)(tht)_2]ClO_4$ obtained (Table 2, line 2.2). If the same precipitating agents are added rapidly to stirred solutions of $[PdR(OClO_3)(tht)_2]$, there is no replacement and the starting neutral perchlorato complex is recovered [39]. Similarly, the reaction of $[Pd(C_6H_3N$=NTo-2,Me-5-*C*,*N*$)Cl(PEt_3)]$ with TlTfO gives the neutral complex $[Pd(C_6H_3N$=NTo-2,Me-5-*C*,*N*$)(OTf)(PEt_3)]$ when the precipitation is rapid, but slow diffusion of *n*-pentane into a CH_2Cl_2 solution leads to the replacement of TfO by water to give $[Pd(C_6H_3N$=NTo-2,Me-5-*C*,*N*$)(OH_2)(PEt_3)]TfO$ (Table 2, line 2.3) [40]. It is possible that the isolation of these aqua complexes requires the formation of HO–H···Y hydrogen bond through a slow process.

2.3. Reactions of water with complexes containing weakly coordinating neutral ligands

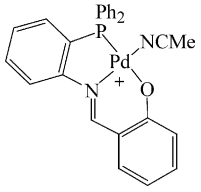
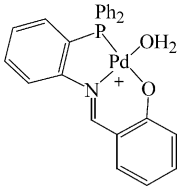
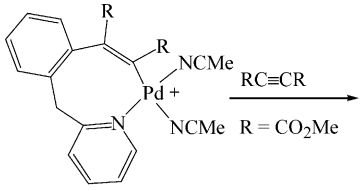
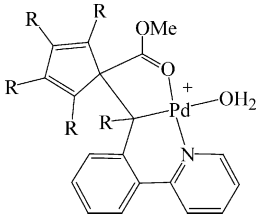
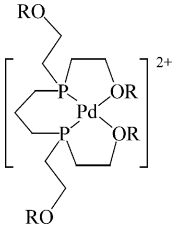
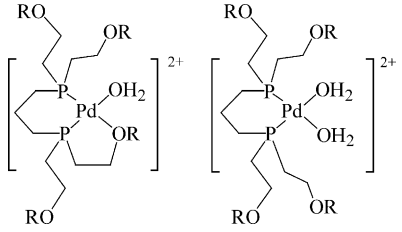
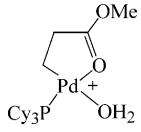
When solvents such as MeCN, acetone, THF or Et_2O are used in the reactions of method given in Section 2.1, cationic solvento complexes can be isolated but frequently recrystallization leads to the replacement of the coordinated solvent by water. Thus, an attempt to grow single crystals of the complex $[Pd(C_6H_3N$=NTo-2-Me-5-*C*,*N*$)(acetone)(PPh_3)]ClO_4$ [41] gives instead the aqua complex $[Pd(C_6H_3N$=NTo-2,Me-5-*C*,*N*$)(OH_2)(PPh_3)]ClO_4\cdot H_2O$ (Table 3, line 3.1) [40].

The complex $[PdL(OH_2)]BF_4$ (Table 3, line 3.2; L = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane) is obtained by diffusion of Et_2O into an MeCN solution of $[PdL(NCMe)]BF_4$ [42]. Upon crystallization of an MeCN complex (Table 3, line 3.3) an aqua complex is obtained [8]. Crystallization of $[Pd\{C_6H_3(CH_2P^tBu_2)_2$-2,6-*C*,*P*,*P*$\}(THF)]BF_4$ (Table 3, line 3.4) produces the aqua complex $[Pd\{C_6H_3(CH_2P^tBu_2)_2$-2,6-*C*,*P*,*P*$\}(OH_2)]BF_4$ [6]. The complex $[PdMe(COD)(OH_2)](SbF_6)$ (Table 3, line 3.5) is obtained by reaction of $[PdMe(COD)(THF)]SbF_6$ with water [43].

On some occasions, when starting from complexes containing two solvento ligands, substitution of one by a neutral ligand occurs concomitantly with the substitution by water of the other. Thus, the reaction of cyclopalladated complexes $[Pd(dmp)(NCMe)_2]ClO_4$ (Table 3, line 3.6) with the ylide Ph_3P=C(H)CONMe$_2$ gives $[Pd(dmp)\{CH(C(O)NMe_2)(PPh_3)\}(OH_2)]ClO_4$ [44]. Similarly, complex $[Pd(N\hat{P})(NCMe)_2](TfO)_2$ (Table 3, line 3.7) reacts with thpy to give $[Pd(N\hat{P})(thpy)(OH_2)](TfO)_2$ [5]. A pincer platinum(II) complex $[Pt(NCN)(PPh_2)]$ (Table 3, line 3.8) reacts with $[Pd(dmp)(NCMe)_2]BF_4$ to afford the dinuclear phosphido-bridged complex $[Pt(NCN)(\mu$-$PPh_2)Pd(dmp)(OH_2)]BF_4$ [45]. When the solvento complex in line 3.9 of Table 3 and $MeO_2CC{\equiv}CCO_2Me$ are heated in ClC_6H_5, two molecules of the alkyne inserts and the MeCN ligands are substituted by a water molecule and the carbonyl oxygen of an ester group [46].

The complex $[PdL](BF_4)_2$ in line 3.10 of Table 3 reacts stepwise with water to give $[PdL(OH_2)](BF_4)_2$ and

Table 3
Synthesis of aqua palladium complexes by reacting water with palladium complexes containing weakly coordinated neutral ligands

Line	Starting palladium complex	Aqua palladium complex	Ref.
3.1	[Pd(R)(acetone)(PPh_3)]ClO_4[a]	[Pd(*R*)(OH_2)(PPh_3)]ClO_4·H_2O	[41]
3.2	[PdL(NCMe)]BF_4[b]	[PdL(OH_2)]BF_4	[42]
3.3			[8]
3.4	[Pd(Ar)(THF)]BF_4[c]	[Pd(Ar)(OH_2)]BF_4	[6]
3.5	[PdMe(COD)(THF)]SbF_6	[PdMe(COD)(OH_2)]SbF_6	[43]
3.6	[Pd(dmp)($NCMe)_2$]ClO_4 + Ph_3P=C(H)C(O)NMe_2	[Pd(dmp){CH(C(O)NMe_2)(PPh_3)}(OH_2)]ClO_4	[44]
3.7	[Pd(NP̂)($NCMe)_2$]$(TfO)_2$[d] + thpy	[Pd(NP̂)(thpy)(OH_2)]$(TfO)_2$	[5]
3.8	[Pt(NCN)(PPh_2)][e] + [Pd(dmp)($NCMe)_2$]BF_4	[Pt(NCN)(μ-PPh_2)Pd(dmp)(OH_2)]BF_4	[45]
3.9			[46]
3.10			[47]
3.11	[Pd($NH_3)_3$(SO_3)]	[Pd($NH_3)_2$(OH_2)(SO_3)]	[48]
3.12	[Pd(η^3-C_3H_5)(OEt_2)(PCy_3)]BAr_4[f] + CH_2=$CHCO_2Me$		[49]
3.13	[PdMe(NCMe)(P∼N)]BF_4[g]	[PdMe(OH_2)(P∼N)]	[50]

[a] R = C_6H_3N=NTo-2-Me-5-*C*,*N*.
[b] L = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane.
[c] Ar = $C_6H_3(CH_2P^tBu_2)_2$-2,6-*C*,*P*,*P*.
[d] NP̂ = *o*-$Ph_2PC_6H_4$-CH=N-^{i}Pr-*C*,*N*.
[e] NCN = $C_6H_3(CH_2NMe_2)_2$-2,6-*C*,*N*,*N*.
[f] Ar = 3,5-$C_6H_3(CF_3)_2$.
[g] P∼N = 6-mesityl-2-{(dimesitylphosphino)methyl}pyridine.

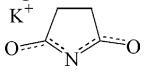
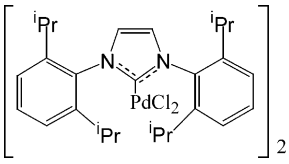
$[PdL(OH_2)_2](BF_4)_2$ [47]. Although NH_3 is strongly bonded to palladium, when [Pd($NH_3)_3$(SO_3)] is steam-distilled until complete dissolution, the complex [Pd($NH_3)_2$(OH_2)(SO_3)] is formed (Table 3, line 3.11) [48]. The η^3-allyl palladium complex [Pd(η^3-C_3H_5)(OEt_2)(PCy_3)]BAr_4 reacts with methyl acrylate at −78 °C to give the complex shown in line 3.12 of Table 3 [49].

Complexes [PdClMe(P∼N)] (Table 3, line 3.13) [P∼N = 6-mesityl-2-{(diarylphosphino)methyl}pyridine] react with $AgBF_4$ in the presence of MeCN to afford the solvento complex [PdMe(NCMe)(P∼N)] when the aryl group is 2-tolyl; however, when the aryl group is mesityl, the aqua complex [PdMe(OH_2)(P∼N)] is obtained, which presumably is due to the substitution of water during the recrystallization [50].

2.4. Reactions of halo palladium complexes with salts of coordinating anions and water

This method of synthesis allowed preparation, in the period 1960–1978, of the first aqua palladium complexes and some of the few reported neutral and anionic species. They were characterized only by elemental analyses and sometimes, by IR spectroscopy. Therefore, their

Table 4
Synthesis of aqua palladium complexes by reacting halo palladium complexes with salts of coordinating anions and water

Line	Starting palladium complex	Other reagents	Aqua palladium complex	Ref.
4.1	$Na_2[PdX_4]$	$2Na(O_2EAr)$ (E = S, Se)	$Na[Pd\{S(O)_2Ar\}_2X(OH_2)]$[a], $[Pd\{Se(O)_2Ar\}_2(OH_2)_2]$[b]	[51,52]
4.2	$PdCl_2$	Ag_2SO_3 (aq)	$[Pd(SO_3)(OH_2)_3]$ or $[Pd(SO_3)(OH_2)_2]$	[48,53]
4.3	$[PdCl_2(NH_3)_2]$	Ag_2SO_3	$[Pd(SO_3)(NH_3)_2(OH_2)]$	[48]
4.4	$[PdCl_2(NH_3)_2]$	Ag_2SO_4	$[Pd(OSO_3)(NH_3)_2(OH_2)]$	[54]
4.5	$PdCl_2$ in HCl		$[Pd(C_4H_4O_2N)_2(OH_2)_2]$	[55]
4.6	$Q_2[PdCl_4]$ (Q = H, K)	Hgu pH ∼ 2.5 (HCl)	*cis*-$[Pd(Hgu)_2(OH_2)_2]Cl_2$	[56,57]
4.7	$[Pd_2(C–N)_2(\mu\text{-}Cl)_2]$[c]	Li(Fmes)	[Pd(C—N)(Fmes)(OH$_2$)]	[58]
4.8		AgAcO	$[Pd(OAc)_2(OH_2)$(carbene)]	[59]
4.9	$[Pd_2(dmp)_2(\mu\text{-}Cl)_2]$	L[d] and $AgClO_4$	$[Pd(dmp)L(OH_2)]ClO_4$	[21]
4.10	$[PdCl_2$(DACH)]	$AgNO_3$	$[Pd(DACH)(OH_2)_2](NO_3)_2$	[71]
4.11	$[PdCl_2L]$[e]	$AgNO_3$ (aq)	$[PdL(OH_2)_2](NO_3)_2$ (aq)	[72]
4.12	$[PdL(OH_2)_2](NO_3)_2$[e]	$NaClO_4$	$[Pd(ONO_2)(OH_2)L]ClO_4·H_2O$	[72]
4.13	$K_2[PdCl_4]$	*trans*-$[Pt(Hampy)_2(NH_2Me)](NO_3)_2$ + excess $AgNO_3$	$[\{Pt(NH_2Me)_2(\mu_3\text{-ampy})_2\}_2Pd_4(NO_3)_6(OH_2)_2](NO_3)_2·3.5H_2O$	[74]
4.14	$[PdCl_2$(dppma)]	$AgNO_3$	$[Pd(NO_3)_2(OH_2)$(dppma)]NO_3	[73]

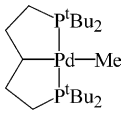
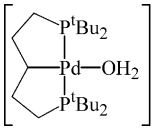
[a] Ar = Ph, X = Cl, Br.
[b] Ar = C_6H_4Y, Y = *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-Me, *p*-NO_2.
[c] C—N = orthometallated *N*,*N*-dimethylbenzylamine, 2-(*p*-tolyl)pyridine, azobenzene, *N*,*N*-dimethyl-1-naphthylamine and 2-benzylpyridine.
[d] L = Mequin, bquin, 2,9-dimethyl-1,10-phenanthroline.
[e] L = 1-methyl-2,2′-bipyridin-3-ylium.

proposed formulations or/and structures should be taken with caution. $Na_2[PdX_4]$ reacts in water with 2 equiv. of $Na(O_2EAr)$ (E = S, Se; Table 4, line 4.1) to give $Na[Pd\{S(O)_2Ar\}_2X(OH_2)]$ (Ar = Ph, X = Cl, Br) [51] or $[Pd\{Se(O)_2Ar\}_2(OH_2)_2]$ (Ar = C_6H_4Y, Y = *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-Me, *p*-NO_2) [52]. $PdCl_2$ reacts with Ag_2SO_3 (Table 4, line 4.2) in water to give a complex formulated as $[Pd(SO_3)(OH_2)_3]$ [48]. However, Eskenazi et al. showed later that the chemical analyses and infrared spectrum of the solid obtained by Earwicker's methods were in agreement with the formula $[Pd(SO_3)(OH_2)_2]$ [53]. The complex $[Pd(SO_3)(NH_3)_2(OH_2)]$ (Table 4, line 4.3) is obtained from $[PdCl_2(NH_3)_2]$ and Ag_2SO_3 [48]. When Ag_2SO_4 is used, the sulfato complex $[Pd(OSO_3)(NH_3)_2(OH_2)]$ (Table 4, line 4.4) is obtained [54]. Mixing a solution of $PdCl_2$ in HCl with succinimide and adjusting the pH to 7 with KOH (Table 4, line 4.5) gives the complex $[Pd(C_4H_4O_2N)_2(OH_2)_2]$ [55]. Similarly, $Q_2[PdCl_4]$ (Q = H, K) reacts with 2 mol of guanosine in water at pH ∼ 2.5 (HCl) (Table 4, line 4.6) to produce *cis*-$[Pd(Hgu)_2(OH_2)_2]Cl_2$ [56,57].

The reactions of cyclometallated complexes $[Pd_2(C–N)_2(\mu\text{-}Cl)_2]$ (C–N = orthometallated *N*,*N*-dimethylbenzylamine, 2-(*p*-tolyl)pyridine, azobenzene, *N*,*N*-dimethyl-1-naphthylamine and 2-benzylpyridine) with Li(Fmes) give (Table 4, line 4.7), after hydrolysis, the first well-characterized neutral aqua complexes [Pd(C–N)(Fmes)(OH$_2$)] [58]. Recently, the synthesis of the neutral carbene complex $[Pd(OAc)_2L(OH_2)]$ (Table 4, line 4.8), generated from AgAcO and $[PdCl_2L]_2$ has been reported [59].

The use of $AgNO_3$ has been described to give nitrato [21,60–70] or aqua [71,72] complexes or a mixture of both [73] or even a complex containing both ligands [72]. Thus, $[Pd_2(dmp)_2(\mu\text{-}Cl)_2]$ reacts with some chelating ligands L (Table 4, line 4.9) and $AgClO_4$ to give complexes $[Pd(dmp)L(OH_2)]ClO_4$. If $AgNO_3$ is used instead, no aqua complex is isolated but [Pd(dmp)(NO_3)L] [21]. Contrarily, abstraction of the chloro ligands in $[PdCl_2$(DACH)] (Table 4, line 4.10) with $AgNO_3$ in water has been reported to give $[Pd(DACH)(OH_2)_2](NO_3)_2$ [71]. Treatment of the cyclopalladated $[PdCl_2L]$ (Table 4, line 4.11) with $AgNO_3$ in water yields a solution containing $[PdL(OH_2)_2](NO_3)_2$ which on evaporation affords $[Pd(ONO_2)_2L]$. Addition of $NaClO_4$ to a water solution of $[PdL(OH_2)_2](NO_3)_2$ (Table 4, line 4.12) gives crystals of $[Pd(ONO_2)(OH_2)L]ClO_4·H_2O$ [72]. The cyclic aqua palladium/platinum complex $[\{trans\text{-}Pt(NH_2Me)_2(\mu_3\text{-}ampy)_2\}_2Pd_4(NO_3)_6(OH_2)_2](NO_3)_2·3.5H_2O$ (Table 4, line 4.13) is obtained in the reaction of *trans*-$[Pt(Hampy)_2(NH_2Me)](NO_3)_2$ with $K_2[PdCl_4]$ and excess $AgNO_3$ [74]. Finally, the reaction of $[PdCl_2$(dppma)] with $AgNO_3$ (Table 4, line 4.14) gives a mixture of $[Pd(NO_3)_2$(dppma)] and $[Pd(NO_3)_2(OH_2)$(dppma)]NO_3 [73]. In conclusion, the use of $AgNO_3$ is not a good method to prepare aqua palladium complexes. If it is used, the X-ray

Table 5
Synthesis of aqua palladium complexes by protonation of anionic ligands with acids in the presence of water (protonolysis)

Line	Starting palladium complex	Other reagents	Aqua palladium complex	Ref.
5.1	$[PdL_2(bpy)]\cdot 4.5H_2O$[a]	$HNO_3 + NaClO_4$	$[PdL(bpy)(OH_2)]ClO_4\cdot H_2O$	[75]
5.2	$[Pd(OAc)_2(dppp)]$	2TsOH	$[Pd(OTs)(OH_2)(dppp)]TsO$	[76]
5.3	[PdR(acac)][b]	$(HPPh_3)ClO_4$	$[PdR(OH_2)_2(PPh_3)]ClO_4\cdot H_2O$	[77]
5.4		$H_2NEt_2(BPh_4)$		[78]
5.5	$Pd(OAc)_2$	$PPh_3 + HX$	*cis*-$[Pd(OH_2)_2(PPh_3)_2]X_2\cdot nH_2O$[c]	[79]
5.6	$[Pd(OAc)(\kappa^2\text{-}OAc)L]$[d]	CF_3CO_2H	$[Pd(O_2CCF_3)_2L(OH_2)]$	[80]

[a] HL = 1-methylthymine.
[b] R = $C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5.
[c] X = TsO, $n = 2$; $MeSO_3$, $n = 0$.
[d] L is the carbene shown in line 4.8.

crystal structure is necessary to be sure of the nature of the isolated complex. In solution, it should not be used if an aqua complex is required.

2.5. Protonation of anionic ligands with acids in the presence of water (protonolysis)

The acid–base reaction $[\{M\}\text{–}Y] + HX + H_2O \rightarrow [\{M\}\text{–}OH_2]X + HY$ is appropriate for the synthesis of an aqua complex if HX is a stronger acid than HY and X is a weakly coordinating anion. Thus, the compound prepared by addition of excess of $NaClO_4$ to an aqueous solution of $[PdL_2(bpy)]\cdot 4.5H_2O$ (HL = 1-methylthymine) and the pH of the solution brought to 6.5 with 0.5 M HNO_3 (Table 5, line 5.1) was assigned to $[PdL(bpy)(OH_2)]ClO_4\cdot H_2O$, on the basis of the elemental analysis data and its IR spectrum. However, recrystallization of this complex from H_2O/acetone gave $[PdL(bpy)]_2(ClO_4)_2$ as the only product [75]. $[Pd(OAc)_2(dppp)]$ (Table 5, line 5.2) reacts with 2 equiv. of TsOH to give the complex $[Pd(OTs)(OH_2)(dppp)]TsO$ [76]. We have reported the synthesis of *cis*-$[PdR(OH_2)_2(PPh_3)]ClO_4\cdot H_2O$ (Table 5, line 5.3) by reacting [PdR(acac)] with $(HPPh_3)ClO_4$ [77]. Protonolysis of the pincer complex in line 5.4 of Table 5 with $H_2NEt_2(BPh_4)$ in wet CH_2Cl_2 produces the corresponding aqua complex [78].

Recently, syntheses have been reported of (i) complexes *cis*-$[Pd(OH_2)_2(PPh_3)_2]X_2\cdot nH_2O$ (Table 5, line 5.5) by reacting $Pd(OAc)_2$, PPh_3 and HX in acetone in the presence of H_2O [79], and (ii) the neutral complex $[Pd(O_2CCF_3)_2L(OH_2)]$ (Table 5, line 5.6), from $[Pd(OAc)(\kappa^2\text{-}OAc)L]$ and CF_3CO_2H. This carbene complex can also be synthesized by reaction of $Pd(O_2CCF_3)_2$ and L [80].

2.6. Protonation of hydroxo complexes

The oxidation by water of the pallada(II)cyclopentane complex $[Pd(CH_2)_4\{(pz)_3BH\}]^-$ gives H_2 and the hydroxo palladium(IV) complex $[Pd(CH_2)_4\{(pz)_3BH\}(OH)]$ [81–83]. This complex forms a hydrogen bond adduct with ArOH (Table 6, line 6.1); a crystal structure has been reported for this aqua palladium(IV) complex $[Pd(CH_2)_4\{(pz)_3BH\}\{O(H)H\cdots OAr\}]$ (see below). No other palladium(IV) aqua complexes are known. The protonation of $[Pd_2(C_6F_5)_2(\mu\text{-}OH)_2L_2]$ with HTfO has been reported to yield the aqua complexes $[Pd(C_6F_5)L(OH_2)_2]TfO$ [84] (Table 6, line 6.2).

$[Pd(SO_3)(OH_2)_n]$, formulated as a triaqua complex by Earwicker [48] and as a diaqua complex by Eskenazi et al. [53] can be prepared by bubbling a stream of SO_2 into an aqueous suspension of palladium hydroxide [48].

2.7. From other aqua palladium complexes

The reactions between the aqua palladium(II) sulfito complexes $[Pd(SO_3)(OH_2)_n]$ ($n = 3$ [48] or 2 [53]) and aqueous ammonia gives $[Pd(SO_3)(NH_3)(OH_2)_2]$ or $[Pd(SO_3)(NH_3)_2(OH_2)]$ (Table 7, line 7.1) depending on the amount of ammonia [48]. The IR spectra of these complexes are in agreement with the presence of an unidentate sulfito group coordinated through sulfur [53]. Recrys-

Table 6
Synthesis of aqua palladium complexes by protonation of hydroxo complexes

Line	Starting palladium complex	Other reagents	Aqua palladium complex	Ref.
6.1	$[Pd(CH_2)_4\{(pz)_3BH\}]^-$	ArOH[a]	$[Pd(CH_2)_4\{(pz)_3BH\}\{O(H)H\cdots OAr\}]$	[82,83]
6.2	$[Pd_2(C_6F_5)_2(\mu\text{-}OH)_2L_2]$	HTfO	$[Pd(C_6F_5)L(OH_2)_2]TfO$[b]	[84]
6.3	$Pd(OH)_2$	SO_2	$[Pd(SO_3)(OH_2)_n]$ ($n = 2$ or 3)	[48,53]

[a] Ar = Ph, C_6F_5.
[b] L = PPh_3, $AsPh_3$.

Table 7
Synthesis of aqua palladium complexes from other aqua palladium complexes

Line	Starting palladium complex	Other reagents	Aqua palladium complex	Ref.
7.1	$[Pd(SO_3)(OH_2)_n]$[a]	NH_3	$[Pd(SO_3)(NH_3)_x(OH_2)_{3-x}]$[b]	[48,53]
7.2	$[PdClX_2(OH_2)]^-$[c]	H_2O	$[PdX_2(OH_2)_2]$	[51]
7.3	$[PdX_2(OH_2)_2]$[c]	NaNCS	$Na[PdX_2(NCS)(OH_2)]$	[51]
7.4	$[Pd(en)(OH_2)_2](ClO_4)_2$	Reduced GSH_2[d]	$[Pd(GS)(OH_2)]_2{\cdot}H_2O$	[85]

[a] $n = 1$ or 2.
[b] $x = 1$, 2.
[c] $X = S(O)_2Ph$.
[d] GSH_2 = glutathione.

Table 8
Synthesis of aqua palladium complexes by reacting inorganic acids with palladium metal or zerovalent palladium compounds

Line	Starting palladium material	Other reagents	Aqua palladium complex	Ref.
8.1	Pd	$HClO_4$	$[Pd(OH_2)_4](ClO_4)_2$	[86]
8.2	Pd	H_2SO_4	$[Pd(O_2SO_2)(OH_2)_2]$	[54]
8.3	$[Pd(PPh_3)_4]$	HX[a]	$[Pd(OH_2)(PPh_3)_3]X_2$	[87]
8.4	$[Pd(PR_3)_2]$[b]	$(H_3O)X$[c]	*trans*-$[PdH(OH_2)(PR_3)_2]X$	[88,89]

[a] $X = ClO_4$, BF_4.
[b] R = ^{t}Bu [88], Cy [89].
[c] $X = HOBF_3$, BF_4.

tallization of $Na[PdCl\{S(O)_2Ar\}_2(OH_2)]$ from water gives $[Pd\{S(O)_2Ph\}_2(OH_2)_2]$ and its reaction with an equimolar amount of sodium thiocyanate (Table 7, line 7.3) in water leads $Na[Pd(NCS)\{S(O)_2Ph\}_2(OH_2)]$ [51]. Upon addition of reduced glutathione GSH_2 to an aqueous solution (pH 2) of *cis*-$[Pd(en)(OH_2)_2](ClO_4)_2$ (Table 7, line 7.4) the complex $[Pd(GS)(OH_2)]_2{\cdot}H_2O$ precipitates [85].

2.8. Reactions of inorganic acids with palladium metal or zerovalent palladium compounds

The aqua palladium complex $[Pd(OH_2)_4](ClO_4)_2$ (Table 8, line 8.1) is obtained by adding perchloric acid to a solution obtained by dissolving palladium sponge in concentrated nitric acid and the solution heated till it fumes strongly. On cooling, the complex is deposited as brown needles which deliquesce in moist air. It is stable in solution only at low pH [86]. When sulfuric acid is used instead of perchloric acid (Table 8, line 8.2), the complex $[Pd(O_2SO_2)(OH_2)_2]$ is obtained [54].

$[Pd(PPh_3)_4]$ is oxidized by aqueous HX ($X = ClO_4$, BF_4) to give $[Pd(OH_2)(PPh_3)_3]X_2$ (Table 8, line 8.3) and one molecule H_2 per mole of palladium [87], while starting from $[Pd(PR_3)_2]$ (R = ^{t}Bu [88], Cy [89]) their reactions (Table 8, line 8.4) with $(H_3O)X$ ($X = HOBF_3$, BF_4) lead to *trans*-$[PdH(OH_2)(PR_3)_2]X$.

2.9. Miscellaneous methods

The complex $[Pt(NH_3)_4][Pd(SO_3)_2(OH_2)]$ (Table 9, line 9.1) is formed from sodium tetrasulfitopalladate(II) and tetraamminaplatinum(II) dichloride [53]. A tetranuclear Pd_3Pt complex (Table 9, line 9.2), *trans*-$[\{trans\text{-}Pt(\mu\text{-}NH_2)_2(\mu_3\text{-ampy-}N^1,N^2,N2')_2\}(en)Pd_2\{Pd(OH_2)\}](NO_3)_4{\cdot}2H_2O$, has been obtained by reaction of $[Pd(en)(OH_2)_2](NO_3)_2$ with *trans*-$[Pt(NH_3)_2(Hampy)_2](NO_3)_2$, adjusting the pH to 8–9 with NaOH [90].

3. Properties of aqua palladium(II) complexes

3.1. Spectroscopic properties

3.1.1. IR spectroscopy

Two types of calculations have been carried out to predict the vibrational frequencies of water in aqua complexes [91]. Absorption bands due to coordinated water are observed in the regions 3647–3168 cm^{-1} ($\nu_{antisym}$(OH) and ν_{sym}(OH) modes, two broad bands, sometimes overlap-

Table 9
Miscellaneous methods

Line	Starting palladium complex	Other reagents	Aqua palladium complex	Ref.
9.1	$Na_6[Pd(SO_3)_4]$	$[Pt(NH_3)_4]Cl_2$	$Q[Pd(SO_3)_2(OH_2)]$[a]	[53]
9.2	$[Pd(en)(OH_2)_2]^{2+}$[b]	$[Pt(NH_3)_2L_2]^{2+}$[c]	$[\{Pt(NH_2)_2L_2\}(en)Pd_2\{Pd(OH_2)\}]^{2+}{\cdot}2H_2O$	[90]

[a] $Q = [Pt(NH_3)_4]$.
[b] Anion = $2NO_3$.
[c] L = Hampy.

ping) [4,7,9,10,21,29,37–39,51,52,58,74,76,78,87–89] and 1630–1610 cm^{-1} (δ(HOH) mode) [9,51,52,58,74,79,88,89]. The band expected around 670 cm^{-1} cannot be assigned with certainty because of the usual presence of other bands in such region. However, some authors have assigned this band in the region 625–590 cm^{-1} [52].

3.1.2. NMR spectroscopy

The ^1H NMR spectra show the protons of the coordinated water molecules in the wide range 0.35–5.16 ppm [6,7,10,17,18,21,22,24,26,33,35,38–40,44–47,50,58,77,79,84,85,89]. When the NMR spectra of complexes [Pd(C–N)(Fmes)(OH_2)] (C–N = dmp, 2-(*p*-tolyl)pyridine, 2-(phenylazo)phenyl, *N*,*N*-dimethyl-1-naphthylamine and 2-benzylpyridine) are recorded at room temperature in wet $CDCl_3$, the protons of water appear in the range 1.70–2.10 ppm, and in dry $CDCl_3$ a downfield shift at 1.8–2.4 ppm occurs that it is a maximum at −60 °C (2.21–2.80 ppm range). These variations have been attributed to a fast equilibrium between aqua ligand and water in the solvent [58]. The ^1H and ^{19}F NMR spectra of *cis*-[Pd(C_6Cl_2-3,5-F_3)$_2$(THF)$_2$] in d_6-acetone at low temperatures have been interpreted assuming the formation of the aqua complexes *cis*-[Pd(C_6Cl_2-3,5-F_3)$_2$$(OH_2)_2$] and *cis*-[Pd($C_6Cl_2$-3,5-$F_3$)$_2$$(OH_2)${$OC(CD_3)_2$}]. The signals appear in the range 4.5–7 ppm [92]. The cationic complexes [Pd(dmp)L(OH_2)]ClO_4 (L = Mequin, bquin) exhibit signals of variable chemical shift [21]. In [Pd(OTs)(OH_2)(dppp)]TsO the protons of the water molecule are not detectable, probably being involved in exchange processes. This lability is likely to be the basis of the high activity in CO/C_2H_4 copolymerization of this complex [76].

^1H and ^{13}C NMR spectroscopies have been used to identify the products and the binding sites of the aqua complexes [Pd(dien)(OD_2)]$(NO_3)_2$ and [Pd(en)$(OD_2)_2$]$(NO_3)_2$ towards peptides, in aqueous solutions as a function of pD [93].

3.1.3. Visible and UV spectroscopy

The visible and UV spectra of aqueous solutions of the square-planar complexes $[PdX_n(OH_2)_{4-n}]^{2-n}$ (X = Cl, Br; n = 0–4) have been recorded and calculated. The variation of blue shift and of band intensity due to the different symmetry of the complexes within each series together with previous magnetic circular dichroism and polarized crystal spectra have made possible unambiguous assignment of the bands in the $[PdX_4]^{2-}$ spectra [94].

The UV–vis spectra of complexes $[Pd(bpy)(OH_2)_2]^{2+}$ $[Pd(OH_2)_2(dppe)]^{2+}$, $[Pd(OH_2)_2(dtco)]^{2+}$, [Pd(OH)$(OH_2)_3]^+$[85], $[Pd(en)(OH_2)_2]^{2+}$ [85,95], and [PdCl$(OH_2)_3]^+$ [96] have been reported.

3.2. Kinetic and reaction mechanisms

The stepwise anations and acid hydrolyses in the palladium(II) chloro and bromo systems have been shown to involve equilibria between species $[PdX_n(OH_2)_{4-n}]^{2-n}$ (X = Cl, Br; n = 0–4) including the *cis* and *trans* isomers for n = 2. However, these equilibria have been the subject of some disagreements between various authors [97,98]. Aqueous solutions of chloro complexes $[PdCl(1,1,4,7,7\text{-}R^5dien)]^+$ (R = H, Me, Et) [99,100] undergo ready hydrolysis. Similarly, complexes [Pd(C_6H_4CR=NOH-2-*C*,*N*)ClL] (L = various pyridines) readily hydrolyze in aqueous solution to afford mixtures of aqua/hydroxo species $[Pd\{C_6H_4(CR{=}NOH)\text{-}2\text{-}C,N\}(OH_n)L]^{(n-1)+}$ [101].

Kinetic and thermodynamic data have been reported for the reactions $[Pd(en)(OH_2)_2]^{2+} + Cl^- \leftrightarrow [PdCl(en)(OH_2)]^+ + H_2O$ and $[PdCl(en)(OH_2)]^+ + Cl^- \leftrightarrow [PdCl_2(en)] + H_2O$, in aqueous solution [95]. Complex formation equilibria have been reported for Cl^-, OH^-, cyclobutane dicarboxylic acid, peptides and DNA unit constituents with $[Pd(DAP)(OH_2)_2]^{2+}$ (DAP = 1,3-diaminopropane), obtained by treating [$PdCl_2$(DAP)] with 2 equiv. of $AgNO_3$ [102]. The coordination of peptides Ser–Pro–His–His–Gly–Gly and $(His)_6$ to [Pd(mida)(OD_2)] ($mida^{2-}$ = *N*-methyliminodiacetate) was studied by ^1H NMR as model reactions for Cu^{II}(iminodiacetate)-immobilized metal-affinity chromatography sites [103]. Complex formation equilibria involving [Pd(bpy)$(OH_2)_2$]$(NO_3)_2$ and the cyclobutanedicarboxylate ligand (cbdca), en and DNA have been investigated. Mixed-ligand complexes of [Pd(bpy)(cbdca)] with inosine, inosine-5′-monophosphate, uracil, uridine and adenine have been studied. The results show ring opening of the cbdca and monodentate chelation of the DNA components [104]. Interactions of *cis*-$[Pd(en)(OH_2)_2]^{2+}$ with microperoxidase-11 in a molar ratio of 1:1 or 2:1 at pH 1.4 were investigated via electrospray mass spectrometry and MS/MS analysis at room temperature and 40 °C with an incubation time of 2 or 3 days [105].

The product of the reaction between [PdCl-$(Et_4dien)](NO_3)$ with $AgNO_3$ has been formulated as [Pd(Et_4dien)(OH_2)](NO_3). The kinetics of water replacement by thiourea and its methyl, ethyl, *n*-butyl, *N*,*N*′-dimethyl, *N*,*N*′-diethyl, *N*,*N*′-di-*n*-butyl and *p*-tolyl derivatives have been studied in water and in the presence of cationic and anionic micelle-forming surfactants. All the reactions are first order with respect to both reactant species [106]. The hydrolysis of $[Pd(dien)(OH_2)]^{2+}$ has been investigated by potentiometry in aqueous $NaClO_4$. Least-squares treatment of the data obtained indicates the formation of mononuclear and μ-hydroxo-bridged dinuclear complexes. The stability constants for $[Pd(dien)(OH)]^+$ and $[Pd_2(dien)_2(OH)_2]^{2+}$ have been determined [107].

The influence of the anionic surfactant sodium dodecyl sulfate on the rate of the complex formation between $[Pd(OH_2)_4]^{2+}$ and glutathione in aqueous solution has been studied [108]. Simple palladium(II) aqua complexes catalyze hydrolytic decomposition of urea to carbon dioxide and ammonia, via N-coordinated carbamic acid as an intermediate. The kinetics and mechanism of the reactions have been reported [109]. The reversible processes $[Pd(OH_2)_{4-n}L]^{2+} + L \leftrightarrow [Pd(OH_2)_{3-n}L_{n+1}]^{2+} + H_2O$ (n = 0,

1; L = MeCN [110], Me_2SO [111]) and $[Pd(OH_2)_4]^{2+} + RCO_2H \leftrightarrow [Pd(O_2CR)(OH_2)_3]^+ + H_3O^+$ [112] have been studied as a function of temperature and pressure in aqueous solution. It has been reported that the complex $[PdMe(COD)(OH_2)](SbF_6)$ is very labile with respect to substitution reactions being impossible to measure its NMR spectra in donating solvents without partial or total exchange of the ligands within a few minutes [43].

The nature of the ligand L in $[PdL(OH_2)_2]^{2+}$ has a profound influence on its acid properties. Thus, at low pH when L is ethylenediamine [95,113], (aminomethyl)pyridine or *N*′-methyl-2,4′-bipyridin-3-ylium [114], the diaqua complex is stable, whereas for L = bpy, the dimer $[Pd_2(bpy)_2(\mu\text{-}OH)_2]^{2+}$ is the stable species [115–117], i.e. under the conditions where $[Pd(bpy)(OH_2)_2]^{2+}$ has been assumed to exist [118]. The acidity and dimerisation constants have been determined for $[PdL(OH_2)_2]^{2+}$ (L = 2-(aminomethyl)pyridine and *N*′-methyl-2,4′-bipyridin-3-ylium) [114]. The acidity of the hydridic hydrogen in $[PdH(OH_2)(PCy_3)_2]BF_4$ is higher than that of the water hydrogen atoms because its reaction with D_2O gives first $[PdD(OH_2)(PCy_3)_2]^+$ and only after a prolonged reaction time $[PdD(OD_2)(PCy_3)_2]^+$ [89].

Kinetics and mechanism of regioselective hydrolysis of amide bonds in various di- and tripeptides by $[Pd(OH)(OH_2)_3]^+$ or $[Pd(en)(OH_2)_2]^{2+}$ have been studied [119].

3.3. Theoretical studies

The low-spin square-planar configuration of complex $[Pd(OH_2)_4]^{2+}$ has been discussed in terms of ligand fields effects [120].

σ-Bond metathesis reactions of water with palladium hydride complexes [Pd(X)(H)(NH_3)(OH_2)] (X = Cl, H) to yield hydrogen have been studied using ab initio molecular orbital methods at the second-order Møller–Plesset (MP2) perturbation level. The calculations show that such reactions are feasible and that they can in some instances be competitive with an oxidative addition/reductive elimination sequence. A key factor is the presence of an additional lone pair not engaged in the initial bonding of the metal atom with the reacting water [121]. A model to fit the complexation and accurate formation constants for the aqua species in solutions of *cis*-dichloropalladium(II) drugs has been proposed [122,123]. DFT calculations support that complexes of the type $[PdL_3(OH_2)]^+$ can be stable only when the water interacts efficiently with the anion [18].

3.4. Crystal structures

The first aqua palladium complex characterized by X-ray crystallography, [Pd(dmp)(bquin)(OH_2)]ClO_4, was reported in 1978 [21]. A total of 53 crystal structures of such complexes have been described. Table 1 shows the name the Cambridge Crystallographic Database (CCD) [124] gives to these complexes, the number of aqua ligands and the nature of the other ligands. The ligand in *trans* to H_2O is marked with an asterisk. Except for the recently reported complexes [Pd(dmp)(Fmes)(OH_2)] (UGILIF) [58] and $[PdX_2L(OH_2)]$ (L = carbene ligand in line 4.8 of Table 4; X = OAc (EKUSUY) [59], X = CF_3CO_2 [80]) all the aqua palladium complexes characterized crystallographically are cationic. As the complex KIPYOX ($[Pd(ONO_2)(OH_2)L]ClO_4{\cdot}H_2O$) contains the cationic ligand L = 1-methyl-2,2′-bipyridinium it can also be considered a "neutral" palladium complex [72]. Particularly significant is the presence in the cationic complexes of weakly coordinating counteranions (TfO^-, ClO_4^-, BF_4^-, BPh_4^-, BAr_4^-, $C_6F_5O^-$, PF_6^-, TsO^-, NO_3^-). Therefore, as we remarked previously, it seems imperative to prepare aqua palladium complexes that anions do not compete with the aqua ligand. In addition, the cationic nature of these complexes seems to contribute to their stability making harder the metal center.

The formal oxidation state of palladium is +2 for all except for ZIJKEI ($[Pd(CH_2)_4\{(pz)_3BH\}\{O(H)H\cdots OC_6F_5\}]$) and REQDEW ($[Pd(CH_2)_4\{(pz)_3BH\}\ \{O(H)H\cdots OPh\}]$) complexes in which it is +4 [82,83]. The latter are members of a family of Pd(IV) compounds that crystallize as adducts with various phenols. One of these adducts is described as an hydroxo complex because the hydrogen bond interaction is of the type Pd–(H)O···H–OTo (i.e., the PdO···H distance is greater than the H–OR length) while for ZIJKEI and REQDEW (R = C_6F_5, Ph) the interaction is Pd–(H)O–H···OR and, therefore, they are best described as aqua complexes. Aqua complexes of a metal in such a high oxidation state are expected to be too acidic to be stable. In fact, all the above adducts could be considered as intermediate between hydroxo and aqua complexes.

Most aqua palladium(II) complexes characterized crystallographically are organometallics, and whenever possible, the aqua ligand prefers to be *trans* to C. Thus, the only cases in which the aqua ligand is not *trans* to C are the palladium(IV) complexes ZIJKEI and REQDEW, because of the facial coordination of the $(pz)_3BH$ ligand, and the palladium(II) complex ENEGEJ, due to the presence of a P–N chelating ligand (see Table 10).

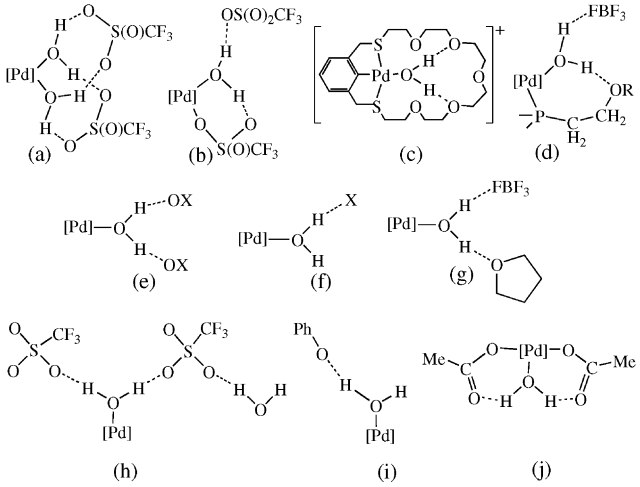
3.4.1. Hydrogen bonding

The importance of hydrogen bonding in the formation and stabilization of aqua transition metal complexes is well documented [18,38,89,128–130]. Thus, *trans*-$[PdH(OH_2)(PCy_3)_2]X$ complexes are obtainable only with fluorine-containing counteranions forming hydrogen bonds with the aqua ligand ($HOBF_3$, BF_4, PF_6), while immediate decomposition to $[Pd(PCy_3)_2]$ occurs when the metathesis of X with BPh_4 or B(*n*-Bu)$_4$ is attempted [89]. Similarly, a cationic pincer aqua palladium complex could only be obtained with the BF_4^- anion while attempts to prepare the $[B\{C_6H_4(SiMe_2R)\text{-}4\}_4]^-$ salt were unsuccessful [18]. However, in the structure of the pincer complex $[Pd\{CH(CH_2CH_2P^tBu_2)_2\}(OH_2)]BPh_4$ (SUHYAV) there are no hydrogen bonds [78].

Table 10
Aqua palladium complexes studied by X-ray diffraction

Complex name (CCD)	Number and nature of ligands[a]								Anions	Ref.
	OH_2	Aryl	Alkyl	P—	N—	S—	O—	Other		
ACIVOX	2			2*					TfO	[29]
AGEWEO	1	1*		2					BF_4	[6]
AGEWIS	1	1*		2					BF_4	[6]
AGIJAB	1			1	1*		1		BF_4	[8]
BQAPPD	1	1*			2				ClO_4	[21]
CUTDAW	2	1*						As*	TfO	[84]
ENEGEJ	1		1	1*	1				BF_4	[50]
EKUSUY	1		1*				2			[59]
FOXFON	1		1*		1		1		TfO	[46]
GUVMOZ	1		1*	2					TsO	[4]
HIPDUF	2	1*		1*					ClO_4	[77]
HUFKUO	1			1*	2				TfO	[5]
IGOVOP	1	1*		1			1		TfO	[26]
ILAQUH	2				2*				NO_3	[125]
KIPYOX	1	1*			1		1		ClO_4	[72]
KUWFUD	1			1				B*	BF_4	[10]
KUZSAZ	1	1*				2			ClO_4	[39]
LISCEV	1			2*			1		BF_4	[47]
MAXJAW	1				2			Pt*	NO_3	[90]
MOTDII	1	1*			2				BF_4	[9]
NATTEH	2			2*	2				BF_4	[32]
NATTIL	2			2*					BF_4	[32]
NUFNOR	1	1*	1		1				ClO_4	[44]
OGILAR	2			2*					TfO	[31,126]
OGILEV	2			2*					TfO	[31]
QEFVEC	1	1*		1	1				PF_6	[7]
RAWPEK	1			2*			1		TfO	[35]
REQDEW	1		2		3*				PhO	[83]
RETJIJ	1				2*		1		NO_3	[74]
RUNDEJ	1	1*		1	1				TfO	[40]
RUNDIN	1	1*		1	1				ClO_4	[40]
SUHYAV	1		1*	2					BPh_4	[78]
TAKDAK	1			2				H*	BF_4	[89]
TETPOK	1		1*	1			1		BAr_4	[49]
TOTKOC	1	1*			2				ClO_4	[36]
UGILIF	1	2*			1					[58]
UKAGUI	1				2*		1			[127]
VETBEB	1	1*			2				BF_4	[11]
XEKXUG	1	1*			2				TfO	[27]
XIQCAB	1	1*				2			PF_6	[23]
XUVJON	1			2*	1				TfO	[34]
XUVJUT	1			2*	1				TfO	[34]
YOSVOR	1			2*			1		TfO	[38]
YOSVUX	2			2*					TfO	[38]
ZEQFAC	1	1*				2		Ag	TfO	[25]
ZESXOK	1	1*		1	1				BF_4	[45]
ZIDZER	1	1*				2			BF_4	[42]
ZIJKEI 10	1		2		3*				C_6F_5O	[82,83]
ZUFGEM	1			2*			1		TsO	[76]
$[Pd(NCN)(OH_2)]^{+}$[b]	1	1*			2				BF_4	[18]
$[Pd(O_2CCF_3)_2L(OH_2)]$[c]	1		1*				2			[80]
$[Pd(OH_2)_2(PPh_3)_2]^{2+}$	2			2*					TsO	[79]
$[Pd(OH_2)_2(PPh_3)_2]^{2+}$	2			2*					$MeSO_3$	[79]

[a] The ligand in *trans* to H_2O is marked with an asterisk.
[b] NCN = $C_6H_3(CH_2NMe_2)_2$-2,6.
[c] L = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

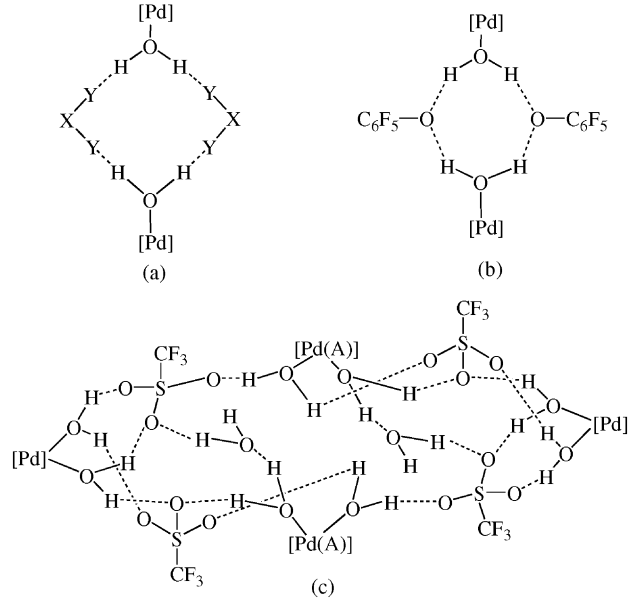


Scheme 2. (a) [29,31,38]; (b) [38]; (c) [42]; (d) [47]; (e) (X = NO_2) [90], (X = TfO) [5], (X = C_4H_{10}) [49]; (f) (X = FBF_3) [10], (X = TfO) [26]; (g) [6]; (h) [34]; (i) [83]; (j) [59].

A search in the CCD shows inter and intramolecular hydrogen bonds involving the aqua ligand lead to monomeric, dimeric, tetrameric or catena structures as shown in Schemes 2–4 [124].

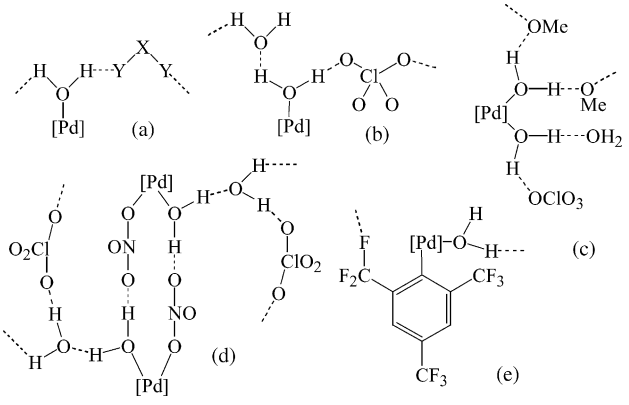
3.4.1.1. Monomers. In the diaqua complexes $[Pd(OH_2)_2L](TfO)_2$ (L = dppp [38], $(PPh_3)_2$ [29], dppf [31]), each aqua ligand is doubly hydrogen-bonded to oxygen atoms of two different triflate anions (Scheme 2a). In the complex [Pd(OTf)(OH_2)(dppp)]TfO [38], the hydrogen atoms of the aqua ligand form two contacts, intramolecularly with an oxygen of the coordinated anion and intermolecularly with an oxygen of the counterion (Scheme 2b). The two hydrogen atoms of the aqua ligand in the complex $[PdL(OH_2)]BF_4$ (L = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane) show intramolecular hydrogen bonding with the peripheral oxygen (Scheme 2c) [42]. The hydrogen atoms of the aqua ligand in the complex [Pd{1,3-bis[di(2-*tert*-butoxyethyl)phosphino]propane-*O*,*P*;*O*′,*P*′}(OH_2)]$(BF_4)_2$ contact intramolecularly with a peripheral oxygen atom and intermolecularly with a fluoride of the counterion [47] (Scheme 2d). In [{*trans*-Pt(μ-NH_2)$_2$(μ$_3$-ampy-N^1,N^2,$N2'$)$_2$}(en)Pd_2{Pd(OH_2)}]$(NO_3)_4$·$2H_2O$ [90] and [Pd(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr-*P*,*N*)(thpy)(OH_2)](TfO)$_2$ [5] the aqua hydrogen atoms are connected by hydrogen bonds to oxygen atoms of two counterions. However, in the complex [Pd($CH_2CH_2CO_2$Me-*C*,*O*)(OH_2)(PCy_3)]BAr_4·$2Et_2O$ (Ar = 3,5-$C_6H_3(CF_3)_2$) [49] they are connected to oxygen atoms of two Et_2O molecules but not with the counterion (Scheme 2e). In the complexes [2-(OH_2)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]BF_4 [10] and [Pd{C_6H_4C(O)Me-2-*C*,*O*}(OH_2)(PPh_3)]TfO [26], an aqua hydrogen is linked to a fluoride or oxygen atom of the counterion, respectively (Scheme 2f). Two crystalline forms of $[Pd(OH_2)L]BF_4$ (L = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane) have been reported. In one of them, one aqua hydrogen contacts with one fluoride of the anion and the other with the oxygen of THF (Scheme 2g) [6]. In the other form, the hydrogen bonds lead to a dimer (see below). In the complex [Pd(NCMe)(OH_2)(BINAP)](TfO)$_2$·H_2O [34] the aqua ligand is connected with two counteranions and one of them is connected to a water molecule of crystallization (Scheme 2h). The analysis of the hydrogen-bonding interaction and the C–O distances in the complex [Pd(CH_2)$_4${($pz)_3$BH}(OH)]·2PhOH are consistent, according to the criterion followed by Canty et al. [83] with the assignment of the adduct as a hydroxopalladium(IV) complex. However, in the CCD it is archived as an aquapalladium(IV) complex and following this and our criteria the complex is better formulated [Pd(CH_2)$_4${($pz)_3$BH}{O(H)H···OPh}] (Scheme 2i).

In the neutral complex $[Pd(OAc)_2L(OH_2)]$ (L = carbene ligand, Table 4, line 4.8) [59], two intramolecular contacts between both hydrogen atom of the aqua ligand and oxygen atoms of the two acetato ligands are observed (Scheme 2j).



Scheme 3. (a) X = ClO_2, Y = O [36]; X = BF_2, Y = F [6,11,89]; (b) [82,83]; (c) [84].

3.4.1.2. Centrosymmetric dimers and tetramers. One of the crystalline forms of $[Pd(OH_2)L]BF_4$ (L = 5,8,11,14,17-pentaoxa-2,20-dithia[21]-*m*-cyclophane) [6] shows both aqua hydrogen atoms contacting two different BF_4^- anions, constituting a centrosymmetric dimer in the solid state (Scheme 3a). The same molecular packing is observed in complexes $[PdH(OH_2)(PCy_3)_2]BF_4$ [89], [Pd(MeOazb)(NCPh)(OH_2)]ClO_4 [36], [Pd{2,6-bis(pyrazol-1-ylmethyl)phenyl-*C*,*N*,*N*}(OH_2)]BF_4 [11]. The analysis of the hydrogen-bonding interaction in the adduct [Pd(CH_2)$_4${($pz)_3$BH}(OH)]·$2C_6F_5OH$ is in accordance with the assignment of [Pd(CH_2)$_4${($pz)_3$BH}{O(H)H···OC_6F_5}] as an aqua palladium(IV) complex containing $C_6F_5O^-$ counteranions. Strong interactions are established via each



Scheme 4. (a) X = S(O)CF_3, Y = O [40]; X = PF_4, Y = F [23]; X = BF_2, Y = F [18]; (b) [40]; (c) [77]; (d) [72]; (e) [58].

hydrogen atom of two aqua ligands and the O atoms of $C_6F_5O^-$, thus constituting a centrosymmetric dimer in the solid state (Scheme 3b) [82,83]. The packing in the complex $[Pd(C_6F_5)(AsPh_3)(OH_2)_2]TfO{\cdot}0.5H_2O$ [84] involves several hydrogen bonds, constituting a centrosymmetric tetramer $[Pd(C_6F_5)(AsPh_3)(OH_2)_2]_4(TfO)_4{\cdot}2H_2O$ (Scheme 3c).

3.4.1.3. Infinite chains. The crystal structure of the complex $[Pd(C_6H_3N{=}NTo\text{-}2,Me\text{-}5\text{-}C,N)(OH_2)(PEt_3)]TfO$ [40] shows interactions between the anion and the aqua ligands giving a catena structure (Scheme 4a). The same motif is observed in complexes $[Pd\{C_6H_3(CH_2SBu^t)_2\text{-}2,6\text{-}C,S,S\}(OH_2)]SO_4$ [23] and $[Pd\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}C,N,N\}(OH_2)]BF_4$ [18]. In the complex $[Pd(C_6H_3N{=}NTo\text{-}2,Me\text{-}5\text{-}C,N)(PPh_3)(OH_2)]ClO_4{\cdot}H_2O$ [40] the aqua hydrogen atoms are connected to the oxygen of the water of crystallization and to the anion to give a polymer (Scheme 4b). In the diaqua complex *cis*-$[PdR(OH_2)_2(PPh_3)]ClO_4{\cdot}H_2O$ ($R = C_6(NO_2)_2\text{-}2,6\text{-}(OMe)_3\text{-}3,4,5$) [77] an infinite chain is formed through intermolecular OH···OMe hydrogen bonds. The aqua ligand *trans* to the phosphine is connected with two methoxy groups of two neighbor molecules and the other aqua ligand is hydrogen-bonded to an oxygen atom of the anion and to the water of crystallization (Scheme 4c). In the complex $[Pd(ONO_2)(OH_2)L]ClO_4{\cdot}H_2O$ (L = 1-methyl-2,2′-bipyridin-3-ylium) [72] hydrogen bonds involving one aqua hydrogen and one nitrato oxygen lead to a centrosymmetric dimer. The other aqua hydrogen contacts with the water of crystallization, which in turn connects with the counteranion and this with a neighbor cation giving a catena structure (Scheme 4d). In the complex [Pd(dmp)(Fmes)(OH_2)] [58], intermolecular contact between a hydrogen atom of the aqua ligand and a fluoride atom of a *o*-CF_3 group of a neighbor molecule leads to a polymer (Scheme 4e).

The mean values of the O···H–O and F···H–O angles in O···HO(H)–Pd and F···HO(H)–Pd hydrogen bonds are 165.164 and 157.617°, respectively. There are 26 structures with 64 O···HO(H)–Pd hydrogen bonds with O···O distances in the range 2.465–2.938 Å. In these structures, the shortest contact occur with the anion in the palladium(IV) complexes REQDEW [83] ($[Pd(CH_2)_4\{(pz)_3BH\}\{O(H)H{\cdots}OPh\}]$, 2.465 Å, 170.20°) (Scheme 2i) and with the water of crystallization in HIPDUF [77] (*cis*-$[PdR(OH_2)_2(PPh_3)]ClO_4{\cdot}H_2O$, $R = C_6(NO_2)_2$-2,6-$(OMe)_3$-3,4,5, 2.536 Å, 171.09°; Scheme 4c). There are eight structures with only 10 F···HO(H)–Pd hydrogen bonds with O···F distances in the range 2.704–2.982 Å. The mean F···O distance (2.835 Å) is longer than the mean O···O value (2.703 Å). Since fluorine has a smaller van der Waal's radius than oxygen [131], it might be concluded that the interactions F···HO(H)–Pd are generally weaker than the corresponding O···HO(H)–Pd. This is in agreement with the results of other studies [132].

3.4.2. Pd–O distances

The Pd–O distances *trans* to carbon donor ligands are in the range 2.097–2.220 Å (mean of 29 values, 2.151 Å) [4,6,9,11,18,21,23,25–27,36,39,40,42,45,46,49,50,58,59,72,77,79,80,84]. The only exception is $[Pd\{CH(CH_2CH_2P^tBu_2)_2\text{-}C,P,P\}(OH_2)]BPh_4$ (2.301 Å) [78]. Although the explanation for this elongation has been based on the steric repulsion exerted for the bulky ^{t}Bu groups, similar pincer complexes shown Pd–O distances within the above range [6,23,78]. This and the fact that the range of Pd–O distances is too broad suggests that this parameter depends not only on the nature of the ligand in *trans* position but also on those in *cis* and, probably, on other causes and, therefore, it is not suitable for make a *trans* influence scale. Thus the Pd–O distances *trans* to P (range: 2.106–2.169 Å; mean of 15 values, 2.136 Å) [5,29,31,32,34,35,38,47,50,76,77,126], *trans* to B (2.208 Å) [10], to N (2.036 Å) [82,83], to As (2.119 Å) [84] to Pt (2.085 Å) [90] and to H^- (2.206 Å) [89] are in the same range as those *trans* to C. The only Pd–O distances out of this range are those *trans* to P of a diphosphine diaqua complex (2.257 and 2.235 Å) [32] or to N in a Pd(IV) complex (1.984 Å) [83] or in the cyclic aqua palladium/platinum complex $[\{trans\text{-}Pt(NH_2Me)_2(\mu_3\text{-}ampy)_2\}_2Pd_4(NO_3)_6(OH_2)_2]\ (NO_3)_2{\cdot}3.5H_2O$ (2.318 Å) [74].

4. Applications of aqua palladium(II) complexes

4.1. Use for the synthesis of other complexes

Due to the weak nature of the Pd–OH_2 bond, aqua complexes are likely good starting materials in coordination chemistry. However, some of the first reports on such potential application were negative. Thus, (i) when $[Pd(OH_2)(PPh_3)_3](ClO_4)_2$ and PPh_3 are melted together $OPPh_3$ and $[PdCl_2(PPh_3)_2]$ are obtained [87], (ii) $[Pd(dmp)L(OH_2)]ClO_4$ (L = Mequin, bquin) does not react

with L but it does with py to give $[Pd(dmp)(py)_2]ClO_4$ [21].

$[Pd\{S(O)_2Ph\}_2(OH_2)_2]$ reacts with 2 equiv. of PPh_3 to give the unexpected complex *trans*-$[Pd(OH)\{S(O)_2Ph\}(PPh_3)_2]$, while chelating ligands give the substitution products $[Pd\{S(O)_2Ph\}_2L_2]$ (L_2 = phen, *o*-phenylenbis(diphenylphosphine)). The anionic complex $Na[PdCl\{S(O)_2Ph\}_2(OH_2)]$ reacts with neutral ligands to give $[PdCl\{S(O)_2Ph\}L_2]$ (L = PPh_3, piperidine, L_2 = phen) or with excess of LiCl to give $Li_2[PdCl_2\{S(O)_2Ph\}_2]$ [51].

The complex $[Pd(OH_2)(dien)](ClO_4)_2$ reacts with 2 equiv. of $Na(BPh_4)$ to give, instead of the expected BPh_4^- salt of the same cation, the phenyl complex $[PdPh(dien)](BPh_4)_2$ and with KOH to give $[Pd(OH)(dien)]ClO_4$ [20].

The complex *cis*-$[Pd(Hgu)_2(OH_2)_2]Cl_2$ reacts with nucleosides (Hnuc), inosine (Hino) or Hgu to give *cis*-$[Pd(nuc)(Hgu)_2]Cl$ (nuc = ino, gu). The same aqua complex transforms into *cis*-$[PdCl_2(guH)_2]$ in HCl solutions (0.5–1N) and into $[Pd(gu)_2]$ at pH 6. Both reactions are reversible and the aqua complex is recovered at pH 2.5 [56,57].

The complex $[Pd(OH_2)_2(dppp)](BF_4)_2$, assumed to be formed by reacting $[PdCl_2(dppp)]$ with $AgBF_4$ in wet methanol, seems to be unstable under neutral conditions. In fact, the addition of Et_2O to its methanol solutions results in the formation of a μ-hydroxo dimer [133]. Cationic complexes *cis*-$[Pd(OH_2)_2(PPh_3)_2]X_2$ (X = TsO; CH_3SO_3) are easily interconverted with the anhydrous neutral complexes *trans*-$[PdX_2(PPh_3)_2]$, depending on temperature and solvent [79].

Trinuclear Pt–Pd–Pt complexes of composition $[L_2Pt(\mu\text{-}X)_2Pd(\mu\text{-}X)_2PtL_2]^{2+}$ ($L_2 = 2NH_3$, en; X = 1-methyluracilato, 1-methylthyminato) have been prepared by mixing aqueous solutions of $[PtX_2L_2]$ and $[Pd(OH_2)_4]^{2+}$. The same reactions but using $[Pd(OH_2)_4]^{2+}$ in 1.3 M HNO_3 solutions lead to $[L_2Pt(\mu\text{-}X)_2Pd(\mu\text{-}X)_2PtL_2]^{3+}$ complexes [75,134]. The aqua ligand in [2-(OH_2)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]BF_4 is easily displaced by other ligands such as CO, isocyanides, MeCN, amines, phosphines, ethers and thioethers to afford the corresponding cationic complexes [10]. The complexes [Pd(C–N)(Fmes)(OH_2)] react with various neutral ligands L to give [Pd(C–N)(Fmes)L] (C–N = dmp, L = 2,6-lutidine, NH_3, PPh_3, ^{t}BuNC, CO, bpy; C–N = orthometallated 2-(*p*-tolyl)pyridine, L = PPh_3) [58].

The complex *trans*-$[Pd(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$ (1-MeC = 1-methylcytosine) reacts with *trans*-$[Pd(NH_3)_2(OH_2)_2](NO_3)_2$ to give *cis*-$[Pd_2(NH_3)_4(\mu\text{-}1\text{-}MeC)_2](NO_3)_2$ in which the two 1-MeC^- ligands are head-to-tail bonded [135]. 1-Methylcytosine platinum(II) complexes react with *trans*-$[Pd(NH_3)_2(OH_2)_2](NO_3)_2$ to give similar dinuclear Pd/Pt complexes with a strong metal–metal bond [136,137]. Theoretical and structural aspects of these complexes were reported later [138].

The thermally unstable hydride *trans*-$[PdH(OH_2)(P^tBu_3)_2]^+$ reacts with MeCN or CO to give the thermally stable *trans*-$[PdH(L)(P^tBu_3)_2]^+$ (L = MeCN, CO) [88]. In the reactions between various N-heterocycles (L) and $[Pd(OH_2)_2(R\text{-}(+)\text{-BINAP})](TfO)_2$, the nature and the distribution of the products have been investigated. The products are diastereomeric $[PdL_2(R\text{-}(+)\text{-BINAP})](TfO)_2$ and $[Pd(OH_2)L(R\text{-}(+)\text{-BINAP})](TfO)_2$ or mixtures of these complexes depending on the nature of L [139].

Positive ion electrospray mass spectrometry has been used to investigate the replacement reactions of *cis*-$[Pd(en)(OH_2)_2]^{2+}$, *cis*-$[Pd(OH_2)_2(dithiacyclootan\text{-}3\text{-}ol)]^{2+}$ and *trans*-$[Pd(pyridine)_2(OH_2)_2]^{2+}$ with sulfur-containing peptides [140]. The substitution of deuterated aqua ligands in $[Pd(pac)(OD_2)]$ and $[Pd_2(pac)(OD_2)_2]$ (pac = 1,6-hexadiamine-*N*,*N*,*N*′,*N*′-tetraacetate, *N*,*N*′-(1,2-ethanediyl)bis(oxy-2,1-ethanediyl)bis[*N*-carboxymethyl glycine]) by inosine or guanosine 5′-monophosphate has been studied [141]. ^{15}N NMR spectroscopy has been used to study the reactions of $[Pd(en)(OH_2)_2]^{2+}$ with NH_3 and glycine [142].

A series of heterometallic cyclophanes, with the general formula *cis*-$[Pd(dppf)(\mu\text{-}L)_2Re(CO)_3Br]_2(OTf)_4$ (L = 4,4′-bpy; 1,2-(4′-dipyridyl)acetylene; 1,4-(dipyridyl)butadiyne), have been prepared from the self-assembly of *cis*-$[Pd(OH_2)(dppf)](TfO)_2$ and $[ReBr(CO)_3L_2]$ [143]. Complexes $[Pd(OH_2)_2L](TfO)_2$ (L = dppp, dppf) were used in combination with the rigid ligand 1,4-bis(4-pyridyl)tetrafluorobenzene to build metallosupramolecular assemblies [126]. Reaction of $[Pd(en)(OH_2)_2](NO_3)_2$ with 2-hydroxypyrimidine (Hpymo) in water results in self-assembly to cyclic complex $[Pd(en)(pymo\text{-}N^1,N^3)]_4(NO_3)_4$ [144].

Aqueous solution of the cationic complex $[Pd_2(NO_3)_n(OH_2)_mL]^{(4-n)+}$ (L = macrocyclic polyamine), obtained by the treatment of $[Pd_2X_2L]X_2$ (X = Cl or I) with $AgNO_3$, is used as a building block for the construction of a tetranuclear palladium complex $[Pd_4(C_2O_4)_2L_2](NO_3)_4$ [145]. Aqueous solutions of complexes formulated as *cis*-$[Pd(N{\sim}N)(OH_2)_2]^{2+}$ (N∼N = (*R*,*R*)-1,2-diaminocyclohexane and (*S*,*S*)-1,2-diaminocyclohexane), obtained by reaction of *cis*-$[PdCl_2(OH_2)_2]$ and $AgNO_3$, were treated with LH (L = 2-hydroxypyrimidine; 4,6-dimethyl-2-hydroxypyrimidine and 4-hydroxypyrimidine) to give a set of enantiomerically pure cyclic polynuclear complexes with the formula *cis*-$[Pd(N{\sim}N)L]_n^{n+}$ (*n* = 4, 6) [125].

4.2. Use as artificial metallo-peptidases and -proteases

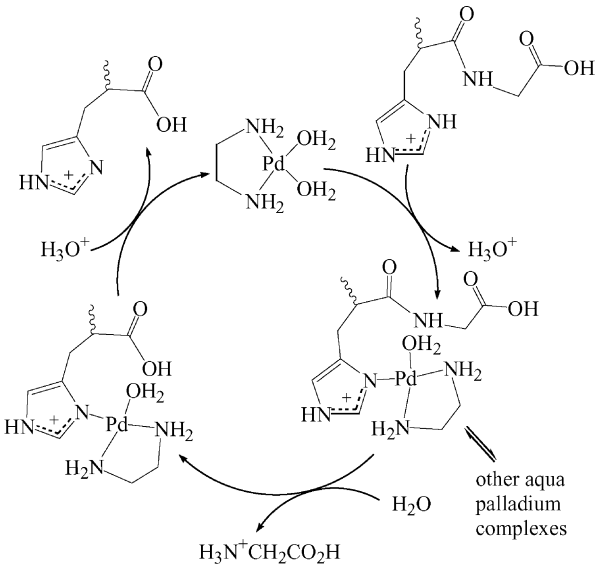
Proteolysis plays functional and regulatory roles in the control of cell cycle, transcription, signal transduction, antigen processing, and apoptosis; it is also a common biochemical procedure in protein sequencing and various new bioanalytical and bioengineering applications. Few enzymes and synthetic reagents are commonly used for selective proteolysis. Proteases are sometimes inadequate because they tend to produce short fragments ill suited for bioanalytical applications, and because proteases themselves contaminate protein digests. In addition, the peptide bond (i.e., the amide group) is extremely unreactive toward hydrolysis, even nonselective

cleavage is hard to achieve. Therefore, new cleavage reagents having improved efficiency and adjustable selectivity working under mild conditions are desired for many emerging applications [146].

Since certain proteolytic enzymes require metal ions for activity, hydrolysis reactions were attempted with different metal complexes [147]. Complexes of palladium(II) meet the requirements just mentioned. In weakly acidic aqueous solutions, Pd(II) ion in several complexes spontaneously binds to methionine residues and to histidine residues [148]. Upon this residue-specific anchoring, the Pd(II) ion promotes hydrolytic cleavage of a proximal peptide bond. Because histidine and methionine have a combined average abundance in proteins of only 4.5%, cleavage directed by them yields relatively long fragments, suitable for bioanalytical applications. Zhu and Kostic working with short peptides have shown that some aqua palladium complexes ($[Pd(OH)(OH_2)_3]^+$, *cis*-$[PdL_2(OH_2)_2]^{2+}$ (L_2 = en, dtco, bpy, dppe) or $[Pd(OH_2)_4]^{2+}$) attach to the sulfur atom of cysteine, *S*-methylcysteine or methionine in peptides after displacement of one or both aqua ligands. This promotes regioselective hydrolysis of the amide bond, under relatively mild conditions, involving the carboxylic group of the amino acid anchoring the metal complex [85,149].

Scheme 5 shows the catalytic cycle for hydrolysis of AcHis–Gly proposed by Parac and Kostic [150,151]. More recently, they have explained the unprecedented selectivity of cleaving synthetic and natural peptides and proteins [152].

Although the X-Pro peptide bond (in which X represents any amino acid residue) in peptides and proteins is resistant to cleavage by most proteolytic enzymes, the complex $[Pd(OH_2)_4]^{2+}$ can selectively hydrolyze this tertiary peptide bond within the X-Pro–Met and X-Pro–His sequence segments. Because Pro–Met and Pro–His sequences are rare in proteins, this sequence-specific cleavage is potentially useful for the removal of the fusion tags from the bioengineered fusion proteins [146].



Scheme 5.

The above comments represent the most recent observations on the subject of this section. Some important steps in the development of this important topic, mostly due to Kostic et al., are the following.

The first report on the application of palladium compounds as metallo-peptidases made use of complexes $[Pd(en)(OH_2)_2]^{2+}$, $[Pd(bpy)(OH_2)_2]^{2+}$, $[Pd(OH_2)_2(dppe)]^{2+}$, $[Pd(OH_2)_2(dtco)]^{2+}$ and $[Pd(OH)(OH_2)_3]^+$. They selectively bind to sulfur atoms in the side chain of methionine and cysteine and selectively promote cleavage of peptide bonds adjacent to these anchoring residues. With $[Pd(OH)(OH_2)_3]^+$ as promoter, the reaction half-lives with some peptides are measured in minutes [85]. The first example of selective hydrolytic cleavage of a protein effected by a metal complex directly attached to the protein was that of cytochrome *c*. It is specifically cleaved at the amide bond His18–Thr19 in the presence of an equimolar amount of $[Pd(OH)(OH_2)_3]^+$ or $[PdL_2(OH_2)_2]^{2+}$ (L_2 = en, dtcol, dtco) [153].

Compounds prepared by reacting $[PdCl_2L_2]$ with $AgNO_3$, formulated as diaqua complexes, promote the hydrolysis of methionine-containing peptides [154,155].

Reactions of aqueous solutions of the hydrolytically active diaqua complexes *cis*-$[PdL(OH_2)]$ (L = *N*,*N* or *S*,*N*-bidentate ligand) with dipeptides glycyl-L-histidine (Gly–His), L-histidylglycine (His–Gly), and the *N*-acetylated dipeptides MeCO–Gly–His and MeCO–His–Gly have been studied by ^{1}H NMR [156]. Complexes $[Pd(OH_2)_4]^{2+}$, *cis*-$[Pd(en)(OH_2)_2]^{2+}$ and *cis*-$[Pd(OH_2)_2(dtcol)]$ effect hydrolytic cleavage of horse myoglobin in aqueous solution [157]. Complexes *trans*-$[PdL(OH_2)_2]^{2+}$ (L = py_2, en or 1,4-diazacycloheptane) cleaved the bovine, pig and chicken albumin; however, complex *trans*-$[Pd(dtco\text{-}OH)(OH_2)_2]^{2+}$ is unreactive [158]. Two molecules of the complex *cis*-$[Pd(en)(OH_2)_2]^{2+}$ lose aqua ligands and bind to His5 and His9 residues in the nonadecapeptide that is the carboxy-terminal segment of the protein myohemerythrin. Only the $[Pd(en)(OH_2)_2]^{2+}$ group bound to His5 cleaves the polypeptide backbone [159].

The complex *cis*-$[Pd(en)(OH_2)_2]^{2+}$ catalyzes the alcoholysis of urea into alkyl carbamate and ammonia [160]. Complexes $[Pd(OH_2)_4]^{2+}$ and $[Pd(en)(OH_2)_2]^{2+}$ act with unprecedented and useful regioselectivity in promoting the hydrolytic cleavage of natural and synthetic peptides and proteins [152]. The reactivity of these aqua palladium complexes have been explored as reagents for regioselective hydrolysis of six natural peptides (chains A and B of insulin, segment 11–14 of angiotensinogen, pentagastrin, angiotensin II, and segment 3–8 of angiotensin II) and two proteins (ubiquitin and cytochrome *c*) [161].

Hydrolytic reactions between various palladium complexes of the type *cis*-$[PdL(OH_2)_2]^{n+}$ (*n* = 2 or 1; L = a chelating diamine ligand, a amino acid or a peptide) and peptides have been studied by ^{1}H NMR spectroscopy [162–164].

The generation of gas-phase palladium(II) complexes, containing deprotonated alanine (A^-) and/or N-terminus derivatized peptides containing histidine as one of the amino acids, by electrospray ionization has been reported. A stable diaqua complex of the formula $[PdA(OH_2)_2]^+$ along with complexes containing A^- and peptide are formed. The collision-induced dissociation patterns of these complexes are in accord with several previous solution-state studies in which Pd(II) caused hydrolysis of peptides at the same position [165].

In a series of works by Ryabov and co-workers, it has been demonstrated that cyclometallated complexes of Pd(II) are functioning as metallo-peptidases [166]. Among the features traditionally ascribed to enzymes, metallacycles display noticeable rate accelerations [167] and stereoselectivity [168]. They manifest the catalytic activity due to facile generation of the aqua/hydroxo ligand *trans* to the σ-bound phenyl ring in aqueous solution [169]. The catalyst precursors are usually chloro complexes containing cyclopalladated acetophenone and 4′-acetylbenzo-15-crown-5 oximes [170,171] and benzylamine derivatives [172], which transform into catalytically active aqua/hydroxo species in aqueous solution. The rate accelerations achieved in some cases are really remarkable [172].

4.3. Other catalytic applications

There is an increasing interest in the use of aqua palladium complexes in organic synthesis. The role of the aqua ligand in these complexes is, in some cases, that of a easily replaceable ligand, in others that of an acid leading to an hydroxo complex. Thus, the aqua hydride complex *trans*-$[PdH(OH_2)(PCy_3)_2]BF_4$ [89] has been used as catalyst for (i) the carbonylation of alkynols to dienoic acids or esters and of alkynediols to cross-conjugated diesters [173], (ii) the carbonylation of α-allenic alcohols to α-vinylacrylic acids in the presence of *p*-toluenesulfonic acid [174]; this reaction is stereoselective in cases where the allene is 1,3-disubstituted and (iii) the hydroesterification of 1,2-polybutadiene. However, it has been reported to be less reactive than $Pd(OAc)_2$ [175]. Probably, the aqua-hydride palladium(II) complex *trans*-$[PdH(OH_2)(PCy_3)_2]BF_4$ acts in these processes as a precursor of $[Pd(PCy_3)_2]$ with the advantage of being an air-stable complex [174].

Aqueous solutions of $[Pd(OH_2)_4]^{2+}$, $[Pd(en)(OH_2)_2]^{2+}$, $[Pd(dien)(OH_2)]^{2+}$, $[Pd(OH_2)_2(MetOMe)]^{2+}$, $[Pd(OH_2)_2(dtcol)]^{2+}$, prepared from the corresponding chloro or iodo complexes and $AgClO_4$, catalyze the selective hydration of nitriles, yielding the corresponding carboxamides [176] and the hydrolytic decomposition of urea into carbon dioxide and ammonia, via N-coordinated carbamic acid as an intermediate, resembling the enzyme urease. The proposed mechanism involves substitution of one aqua ligand to form $[Pd]^{2+}(OH_2)\{O{=}C(NH_2)_2\}$ species followed by formation of complexes $[Pd]^{2+}(OH_2)\{NH_2C(O)NH_2\} \rightarrow [Pd]^{+}(OH)\{NH_2C(O)NH_2\} + H^+ \rightarrow [Pd]^{+}(OH_2)\{NH_2C(O)OH\} + NH_3 \rightarrow [Pd]^{+}(OH_2)_2 + CO_2 + NH_3$ [109].

The selective low-temperature (40–70 °C) catalytic oxidation of methanol, propan-1-ol, and propan-2-ol in the presence of the tetraaquapalladium(II) complex and iron(III) ions and/or molecular oxygen as cooxidants has been studied. The corresponding carbonyl compound is the product of alcohol oxidation. In the reaction mechanism proposed, the key step is palladium(I) formation [177]. The complex $[Pd(OAc)_2L(OH_2)]$ (L is a carbene ligand; Table 4, line 4.8) is an effective catalyst for the aerobic oxidation of alcohols [59]. Recently, the related complex $[Pd(O_2CCF_3)_2L(OH_2)]$ (L is the same carbene ligand), has been used as precatalyst in the hydroarylation of alkynes [80].

Among the applications of aqua palladium compounds in catalysis, the use of aqua diphosphine complexes is of particular importance. Thus, complexes $[Pd(NCMe)(OH_2)(P{-}P)](TfO)_2$ (P–P = several diphosphines) catalyze hydroamination of different olefins [34]. The aqua imine-phosphine complex $[PdMe(OH_2)(Ph_2PC_6H_4N{=}CHPh\text{-}2\text{-}P,N)]BF_4$ promotes the polymerization of ethyl vinyl ether via proton-transfer initiation [24]. The complex [Pd(OTs)(OH2)(dppp)]TsO shows a high catalytic activity in CO/C_2H_4 copolymerization in MeOH (∼6 kg of polymer per g of Pd h) [76]. Recently, it has been reported that in chloroform at room temperature, complex *cis*-$[Pd(OH_2)_2(PPh_3)_2](TsO)_2{\cdot}2H_2O$ catalyzes the carbonylation of ethene to a polyketone; at higher temperature in methanol it catalyzes the hydroesterification of ethene. In both cases, catalysis is accompanied by CO_2 evolution. These results suggest that catalysis occurs via initial formation of a Pd(II)–H species by interaction of H_2O with CO on the metal center though a reaction closely related to that of the water gas shift [79]. Optically active diaqua complexes $[Pd(OH_2)_2\{(P{-}P)\}](BF_4)_2$ (P–P = BINAP, 2,2′-bis(di(*p*-tolyl)phosphino)-1,1′-binaphthyl) are efficient catalysts for asymmetric addition of enol silyl ethers to aldehydes [32,178] and imines [179,180] and for the asymmetric Michael reaction of 1,3-dicarbonyl compounds. The mechanism of the last reaction is quite unique, because the palladium aqua complex allows successive supply of a Brönsted base and a Brönsted acid [181]. The complex $[Pd(PS\text{-}(R)\text{-}BINAP)(OH_2)_2]^{2+}$ (PS-(*R*)-BINAP = the polymer-supported BINAP ligand; Fig. 1) generated from the corresponding dichloro complex and $AgBF_4$ is shown to be a good and reusable

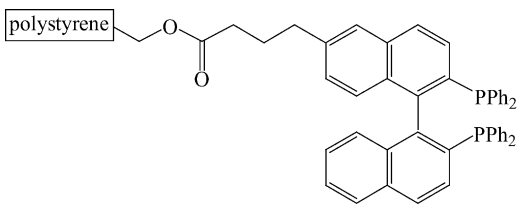


Fig. 1. Polymer-supported BINAP ligand PS-(*R*)-BINAP.

catalyst for asymmetric aldol and Mannich-type reactions [182].

Complexes $[Pd(OH_2)_2(P{-}P)](TfO)_2$ [35], P–P being either *rac*- or *meso*-diphosphine ligands, catalyze the copolymerization of propene and carbon monoxide to isotactic poly(1-methyl-2-oxo-1,3-propanediyl); the meso ligands are more stereoselective than the racemic ligands and display much higher catalytic activity [183]. When P–P = dppf, dppomf, the diaqua complexes are effective catalysts for the methoxycarbonylation of ethene, yet they exhibit quite different selectivity: the dppomf catalyst yields exclusively methyl propanoate, while the dppf catalyst leads to a variety of low molecular weight oxygenates, spanning from methyl propanoate to alternating oligomers of carbon monoxide and ethene [31,184]. The diphosphine complexes $[Pd(OH_2)_nL](BF_4)_2$ ($n = 1$ or 2; $L = R_2P(CH_2)_3PR_2$; $R = CH_2CH_2O^tBu$) are active catalysts in the CO/olefin copolymerization [47]. The complex $[Pd(OH_2)L]X$ (L = 1,3-{bis[(*tert*-butyl)(phenyl)phosphino]methyl}benzene; X = BF_4, TfO) is catalytically active in the aldol condensation of methyl 2-isocyanoacetate and benzaldehyde [17]. The complex $[Pd(NCMe)(OH_2)(BINAP)](TfO)_2$ induces high enantioselectivies in the addition of primary and secondary aromatic amines to α,β-unsaturated oxazolidinones [185]. Recently, cationic diaqua complex $[Pd(OH_2)_2(dppe)]^{2+}$ has been reported to catalyze the addition of arylboronic acids at room temperature and arylsiloxanes at 75 °C to acyclic and cyclic enones [186].

Some pincer aqua palladium complexes are good catalysts. Thus, the following complexes and catalyzed reactions have been reported: (i) dicationic complexes with chiral pyridine bis(oxazoline) ligands for kinetic resolution of racemic styrene tosylaziridines [187], (ii) a series of monoaqua [2,6-bis(2′-oxazolinyl)]palladium complexes for the Michael reaction between α-cyanocarboxylates and methyl vinyl ketone and between acrylonitrile and activated Michael donors, although the enantioselectivities described are modest [27,28], (iii) one of these oxazolinyl complexes, $[Pd\{2,6\text{-bis(i-Pr-oxazolinyl)phenyl}\}(OH_2)](BF_4)$, is a chiral catalysts for the aldol-type condensation of isocyanides and aldehydes in the presence of $i\text{-}Pr_2NEt$ [9], (iv) aqua(2,6-bis[(dimethylamino)methyl]-4-{3-[(1-pyrenyloxy)methyl]-5-(trimethylsilyl)benzyloxy}phenyl)palladium(II) tetrafluoroborate in the aldol reaction between methylisocyanideacetate and aromatic aldehydes [12], (v) $[Pd\{C_6H_3(CH_2SBu^t)_2\text{-}2,6\text{-}C,S,S\}(OH_2)](SO_4)$ is a pH-selective catalyst for the cross-coupling reactions of water-soluble organic halides with organoboron compounds in basic media [23], (vi) P*CP* pincer aqua complexes with P-stereogenic catalyze the aldol condensation of methyl 2-isocyanoacetate and benzaldehyde [17], (vii) some nanosize cartwheel pincer palladium(II) aqua complexes act as Lewis acid catalysts in the double Michael reaction between methyl vinyl ketone and ethyl α-cyanoacetate. NCN′-type pincer complexes were superior to the PCP′- and SCS′-pincer complexes [14,15].

A recent and promising development in the area of catalyst recovery and reuse is the incorporation of a homogeneous catalyst on large frameworks. In this way, macromolecular catalysts are created that can be separated from the product-containing solution by ultra- or nanofiltration techniques. Thus, shape-persistent multi NCN-palladium aqua complexes having two- and three-dimensional geometries were subjected to nanofiltration experiments in order to investigate the influence of rigidity and geometry on the retention of these molecules by membranes [188]. The application of a NCN-pincer palladium(II) aqua complex ($NCN = C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}C,N,N$) as a homogeneous catalyst in a nanofiltration membrane reactor under continuous operating condition has been reported [16,188].

Traces of water have influence in Heck reactions [189–191]. A study has shown that formation of an aqua complex is responsible for the slower rate observed [192].

5. Conclusions

Aqua palladium complexes are important species whose nature and properties have been ignored by many of the authors responsible for their development. We have shown the great variety of methods of synthesis and the reported spectroscopic and chemical properties. The crystal structures show a rich variety of hydrogen bonding interactions. Among the applications of these complexes their use as synthetic intermediates and as catalysts has been highlighted. Two groups of catalytic applications can be distinguished. First, their use as artificial metallo-peptidases and -proteases which is becoming very important because of its efficiency and adjustable selectivity under mild conditions for such important biochemical processes. The number and diversity of other reactions in which aqua palladium complexes are being used is increasing rapidly, e.g. carbonylation of alcohols, hydroesterification of dienes, hydration of nitriles and urea, hydroamination of olefins, polymerization of ethyl vinyl ether, CO/olefin copolymerizations, asymmetric addition of enol silyl ethers to aldehydes, asymmetric Michael and Mannich-type reactions, methoxycarbonylation of ethene, addition of primary and secondary aromatic amines to α,β-unsaturated oxazolidinones, aerobic oxidation of alcohols, etc.

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