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Coordination Chemistry Reviews 249 (2005) 1135–1154

COORDINATION CHEMISTRY REVIEWS

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Review

Aqua palladium complexes: synthesis, properties and applications

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Received 9 July 2004; accepted 8 November 2004
Available online 21 December 2004

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 ($4\text{-}MeC_6H_4SO_3$)

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doi:10.1016/j.ccr.2004.11.005

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.

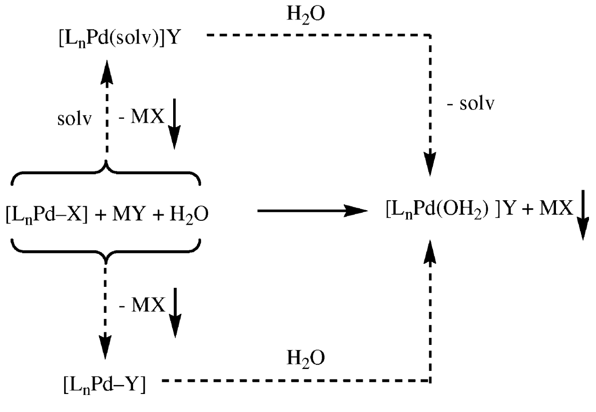
In spite of the great number of aqua complexes and its importance, comprehensive inorganic chemistry collections give a poor view of this field because they only dedicate a short phrase to the $[Pd(OH_2)_4](ClO_4)_2$ complex [1,2] or state that “oxygen-containing solvents such as water, alcohols or ethers 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.