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PREPARATION AND REACTIONS OF HYDROXO-ENYLPALLADIUM(II) DERIVATIVES

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Summary

Some new hydroxo-enyl derivatives of palladium(II) of the type $[Pd(C_7H_8 \cdot OH)Br]_2$, and $[Pd(diene \cdot OH)(L-L)]PF_6$ (C_7H_8 = norbornadiene, diene = norbornadiene or 1,5-cyclooctadiene; L–L = 2,2′-bipyridyl or 1,10-phenanthroline) have been made by nucleophilic attack of H_2O on the diene coordinated to the metal in dipositively charged complexes. Evidence is presented to show that the hydroxo-norbornenyl-1,2-bis(diphenylphosphino)ethane palladium(II) is involved as an intermediate, in an unusual example of oxidation of the alcoholic group through a palladium(II)-mediated intramolecular hydrogen transfer.

Introduction

Complexes containing unsaturated hydrocarbons bonded to transition metals have played a major role in the development of organometallic chemistry, and the nature of the metal–olefin bond has been the subject of numerous studies [1,2]. The reactions of such complexes, namely five-coordination addition [3], replacement of the olefin moiety [4], and nucleophilic attack at the coordinated olefin [5], have been explored in depth and the results, together with structural and spectroscopic data, have provided the basis for advances in theory.

In recent years, since the oxidation of ethylene to acetaldehyde by $PdCl_2$ has been industrially exploited as the Wacker process [6], many organic reactions using palladium complexes have been developed. Of these, much attention has been paid to the reactions of olefins with nucleophiles such as water [7], acetate [8], methanol [9] and amines [10] in the presence of palladium(II), and the mechanism has been extensively studied kinetically as well as by product analysis. Many palladium(II) organometallic derivatives resulting from addition of alcohol, amines and acetate to

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the coordinated olefin ligands, have been isolated and characterized, but only very few examples of water addition have been revealed, by isolation of hydroxy-enyl derivatives [11]. In this paper we report the preparation and the characterization of a new series of hydroxy-enyl complexes of palladium(II) such as $[Pd(C_7H_8 \cdot OH)Br]_2$ and $[Pd(diene \cdot OH)(L-L)]PF_6$ (diene = norbornadiene, 1,5-cyclooctadiene; L-L = 2,2'-bipyridyl, 1,10-phenanthroline). We also describe an unusual example of a palladium(II)-mediated redox intramolecular process in the coordinated norbornenyl moiety which occurs under very mild conditions.

Experimental

Materials. All the starting materials were of commercial origin, except for $Pd(diene)Cl_2$ and $Pd(C_7H_8 \cdot OCH_3)$(1,2-bis(diphenylphosphino)ethane)Cl which were prepared by published procedures [12,13]. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach (Germany).

Preparation of $[Pd(C_7H_8 \cdot OH)Br]_2$, di-µ-bromo-bis(6-hydroxy-2-norbornene-endo-5σ,2π)palladium(II)

A suspension of 199 mg of $Pd(C_7H_8)Cl_2$ in 20 ml of water was treated at room temperature with 251 mg of $AgNO_3$. The AgCl was filtered off and 75.9 mg of NaBr were added to the solution. A green yellow precipitate was obtained on addition of 62 mg $NaHCO_3$, and was recrystallized from methylene chloride and petroleum ether.

Anal. Found: C, 28.64; H, 3.07; O, 5.33; Br, 27.18; Pd, 35.89. PdC_7H_9OBr calcd.: C, 28.52; H, 3.08; O, 5.43; Br, 27.13; Pd, 36.13%.

Preparation of $[Pd(diene \cdot OH)(L-L)]PF_6$ complexes

General procedure. $Pd(diene)Cl_2$ and $AgNO_3$ were mixed in 1/2 molar ratio in water at room temperature. The AgCl was filtered off and an equimolar amount of L-L and of NH_4PF_6 added, to give $[Pd(diene \cdot OH)(L-L)]PF_6$ complexes. The following were prepared in this way:

$[Pd(C_8H_{12} \cdot OH)(Bipy)]PF_6$. (2,2'-Bipyridyl)(1-hydroxycycloocta-4-ene-8σ,4π)-palladium(II) hexafluorophosphate, pale yellow (low yield).

Anal. Found: C, 40.66; H, 3.99; N, 5.34. $PdC_{18}H_{21}N_2OPF_6$ calcd.: C, 40.58; H, 3.97; N, 5.25%.

$[Pd(C_8H_{12} \cdot OH)(1,10\text{-phenanthroline})]PF_6$. (1,10-Phenanthroline)(1-hydroxycycloocta-4-ene-8σ,4π)palladium(II) hexafluorophosphate, white (low yield).

Anal. Found: C, 43.24; H, 3.89; N, 5.24. $PdC_{20}H_{21}N_2OPF_6$ calcd.: C, 43.14; H, 3.80; N, 5.03%.

$[Pd(C_7H_8 \cdot OH)(Bipy)]PF_6$. (2,2'-Bipyridyl)(6-hydroxy-2-norbornene-*endo*-5σ, 2π)-palladium(II) hexafluorophosphate, pale yellow.

Anal. Found: C, 39.67; H, 3.19; N, 5.55. $PdC_{17}H_{17}N_2OPF_6$ calcd.: C, 38.51; H, 3.31; N, 5.42%.

$[Pd(C_7H_8 \cdot OH)(1,10\text{-phenanthroline})]PF_6$. (1,10-Phenanthroline)(6-hydroxy-2-norbornene-*endo*-5σ,2π)palladium(II) hexafluorophosphate, white.

Anal. Found: C, 41.80; H, 3.04; N, 5.40. $PdC_{19}H_{21}N_2OPF_6$ calcd.: C, 42.20; H, 3.16; N, 5.18%.

Preparation of [Pd($C_7H_8 \cdot OCH_3$)(1,2-bis(diphenylphosphino)ethane)]PF_6

(1,2-Bis(diphenylphosphino)ethane)(6-methoxy-2-norbornene-*endo*-5σ,2π)palladium(II) hexafluorophosphate. A suspension of 347 mg of Pd($C_7H_8 \cdot OCH_3$)(1,2-bis(diphenylphosphino)ethane)Cl, (1,2- bis(diphenylphosphino)ethane)(5- methoxynortricyclenyl)palladium chloride in 20 ml of methanol was treated at room temperature with 132 mg of $AgNO_3$. The AgCl was filtered off and the solution stored at −20°C to give the pale-yellow [Pd($C_7H_6 \cdot OCH_3$)(1,2- bis(diphenylphosphino)ethane)]PF_6.

Anal. Found: C, 52.88; H, 4.67. $PdC_{34}H_{35}OP_3F_6$ calcd.: C, 52.78; H. 4.52%.

Preparation of Pd(C_7H_9O)(1,2-bis(diphenylphosphino)ethane)Cl

1,2-Bis(diphenylphosphino)ethane)(norbornanone)palladium(II) chloride.

A suspension of 350 mg of Pd($C_7H_8 \cdot OCH_3$)(1,2-bis(diphenylphosphino)-ethane)Cl(1,2-bis(diphenylphosphino)ethane)(5-methoxynortricyclenyl)palladium chloride in a mixture of 18 ml methanol and 2 ml of water was treated under nitrogen with 88.4 mg of $AgNO_3$. The mixture was filtered and, after treatment with charcoal the solution was treated with 0.52 mmol of HCl to give the white Pd(C_7H_8O)(1,2-bis(diphenylphosphino)ethane)Cl.

Anal. Found: C, 61.04; H, 5.00; Pd, 16.30; Cl, 5,62; MW 623.00. $PdC_{33}H_{34}OP_2Cl$ calcd.: C, 61.16; H, 4.91; Pd, 16.43; Cl, 5.48%; MW 635.40.

The same compound was also prepared by the following procedure. A solution of 182 mg of [Pd($C_7H_8 \cdot OH$)Br]$_2$di-μ-bromo-bis(6-hydroxy-2-norbornene-*endo*-5σ,2π) in CH_2Cl_2 was treated with 245 mg of 1,2-bis(diphenylphosphino)ethane. The solution was treated with charcoal, then mixed with petroleum ether to give a white-brown precipitate, 69 mg of which treated in methanol with 16.8 mg of $AgNO_3$. Addition of 5.8 mg of NaCl to the filtrate caused a slow precipitation of a white compound, which was identified from its IR spectrum as Pd(C_7H_8O)(1,2-bis(diphenylphosphino)ethane)Cl.

Acid cleavage of Pd(C_7H_9O)(1,2-bis(diphenylphosphino)ethane)Cl

An aqueous suspension of this compound was treated with concentrated aqueous HCl overnight. Pd(1,2-bis(diphenylphosphino)ethane)Cl_2 was formed. The organic species was extracted with $CHCl_3$, and identified by GLC analysis as 2-norbornanone.

Physical measurements

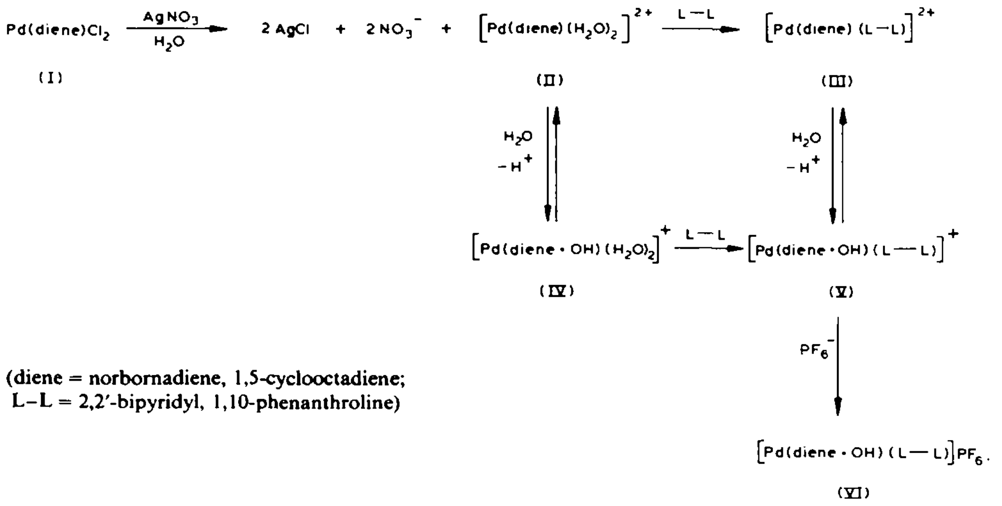
IR spectra were recorded as Nujol mulls (CsI discs on a Perkin-Elmer 457 spectrophotometer). ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker WP 80 FT(80 MHz) recording spectrophotometer. GLC analysis was performed by a C. Erba apparatus. The product 2-norbornanone was identified by comparison of its retention time with that of an authentic sample. Identity was considered to be established by identical retention times on two columns, one capillary and the other packed, both having as stationary phase Silicone oil SE-30.

Results and discussion

When a suspension of Pd(C_7H_8)Cl_2 in water was treated with $AgNO_3$ in a 1/2 ratio AgCl separates and addition of NaBr, gives the green-yellow [Pd($C_7H_8 \cdot$

$OH)Br]_2$. The Pd(diene · OH)(L–L)]PF_6 complexes can be isolated by a similar procedure, as depicted in Scheme 1.

SCHEME 1



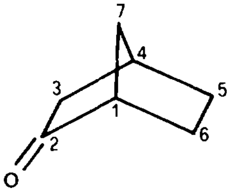
(diene = norbornadiene, 1,5-cyclooctadiene;
L–L = 2,2′-bipyridyl, 1,10-phenanthroline)

Coordinated diene ligands in neutral complexes readily undergo nucleophilic attack; in our case the reactivity of the coordinated olefinic carbon towards water should be enhanced by the dipositive charge of complexes II and III. Similar behaviour was previously noted for analogous reactions with methanol [14]. It has also been reported that, with a few exceptions, coordinated dienes undergo a nucleophilic *trans*-attack at the olefinic carbon. Although we could not carry out a stereochemical study on $[Pd(C_7H_8 \cdot OH)Br]_2$ and [Pd(diene · OH)(L–L)]PF_6 complexes, it is reasonable to assume that the hydroxy-enyl derivatives described result from an *exo*-attack by H_2O.

The IR spectrum of $[Pd(C_7H_8 \cdot OH)Br]_2$ shows a broad band, centered at 3300 cm^{-1}, due to the OH stretching vibration. The same band is sharper and at higher frequencies (~ 3600 cm^{-1}) in the IR spectra of cationic [Pd(diene · OH)(L–L)]PF_6 complexes. Characteristic bands of PF_6 at 835 cm^{-1} (broad vs) and 560 cm^{-1} (s) are also observed for all hexafluorophosphate derivatives. In the case of bipyridyl complexes, the ring vibration stretching frequency at 1576 cm^{-1} of the free ligand is split into two bands and shifted towards higher frequencies. This kind of coordination effect was previously reported for similar transition metal bipyridyl complexes [15].

Reactions of enyl derivatives $[Pd(diene \cdot OCH_3)(L–L)]^+$ with acids yield $Pd(L–L)Cl_2$ complexes [14]. However the nortricyclenyl compound, $Pd(C_7H_8 \cdot OCH_3)(P–P)Cl$, (P–P = 1,2-bis(diphenylphosphino)ethane) after quantitative removal of the chloride with $AgNO_3$, reacts with equimolar amounts of HCl to give a white compound whose IR and ^{13}C NMR spectra (vs band centered at 1750 cm^{-1} and carbon resonance at 220 ppm) are strongly suggestive of the presence of a carbonyl group in the coordinated organic moiety. Acid cleavage of an aqueous suspension of the white compound yielded $Pd(P–P)Cl_2$ and an organic product which, after extraction with chloroform, was indentified by GLC analysis as 2-

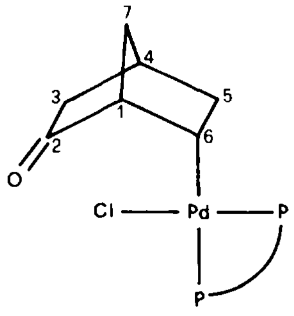
norbornanone:



(VIII)

The ^{13}C NMR spectrum of the white organometallic compound presents six signals, in addition to the resonances of the coordinated 1,2-bis(diphenylphosphino)ethane and the carbonyl resonance at 220 ppm. In particular the doublet of doublets at 23 ppm is fully consistent with carbon atom σ-coordinated to palladium(II) and coupled to two non-equivalent phosphorus atoms, *trans* and *cis*, respectively to it (J_A(P) 24.3 cps; J_B(P) 10.7 cps).

Unfortunately comparison of the ^{13}C NMR spectrum of the organometallic compound, with that of an authentic sample of norbornanone [16] did not clearly reveal which carbon was coordinated to the palladium. The chemical shifts of C(6) and C(5) carbon atoms in the organic moiety are rather close and, in principle, both could be shifted to 23 ppm by coordination. In the absence of definitive evidence, on the basis of the ^{13}C chemical shifts, the coordination of the C(6) carbon atom seems more likely, and we propose the following structure:



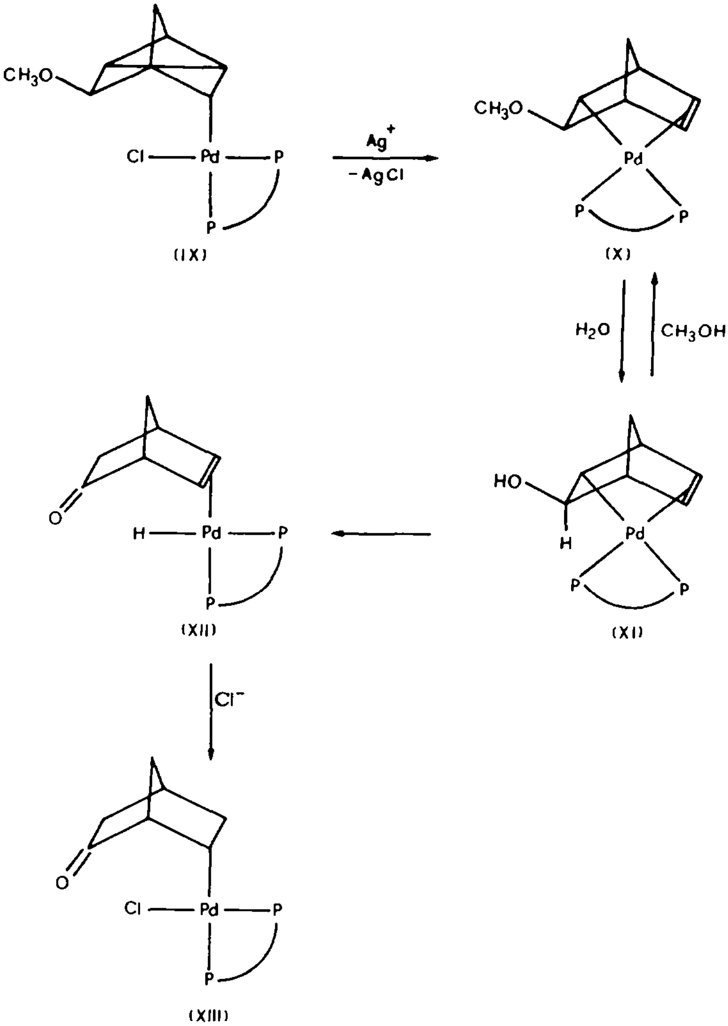
(XIII)

MW measurements and ^1H NMR spectra also agree with the proposed formulation.

A possible mechanism which accounts for the observed internal redox reaction is depicted in Scheme 2. Such a mechanism is based on two features commonly observed in many organometallic and catalytic processes, namely: (i) nucleophilic attack at a coordinated double bond, and (ii) β-hydride elimination from an alkyl chain.

This mechanism involves initial abstraction of the chloride from the substrate (IX), followed immediately by acid-catalyzed reversible reaction giving an equilibrium between the methoxo (X) and the hydroxo-enyl (XI). Subsequently the hydroxo-norbornenyl intermediate XI is converted, through a β-hydride elimination, into the *cis*-hydride π-olefin palladium(II) complex XII, which finally gives the norbornanone organometallic derivative XIII by insertion of olefin into the palladium-hydrogen bond.

SCHEME 2



The occurrence of the first step of the mechanism is supported by the isolation of the hexafluorophosphate salt of X on adding $AgPF_6$ to a methanolic suspension of IX. Moreover the bridge splitting reaction of the hydroxo-bromide dimer $[Pd(C_7H_8 \cdot OH)Br]_2$ with 1,2-bis(diphenylphosphino)ethane followed by abstraction of the chloride with $AgNO_3$ in aqueous methanol and subsequent addition of an equimolar amount of LiCl also affords the product XIII. This suggests that the reaction (Scheme 2) leading to the norbornanone derivative VIII involves a hydroxo-enyl intermediate, in agreement with the proposed mechanism. The subsequent steps in the reaction sequence depicted in Scheme 2 involve the oxidation of the alcohol group and hydride migration to the olefinic carbon. This oxidation is related to the Wacker process, which is thought to occur through β-elimination reactions which give very low, but kinetically significant amounts of palladium hydrides [17]. By analogy, we suggest the formation of the metal hydride XII from the hydroxo-enyl derivative XI; in the present reaction however the presence of the adjacent olefin permits a fast hydride migration to the olefinic bond, which prevents decomposition to metallic palladium.

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