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THE PALLADIUM(II) CATALYZED OLEFIN CARBONYLATION REACTIONS. THE STEREOCHEMISTRY OF THE HYDROXYPALLADATION OF CYCLOOCTADIENE *

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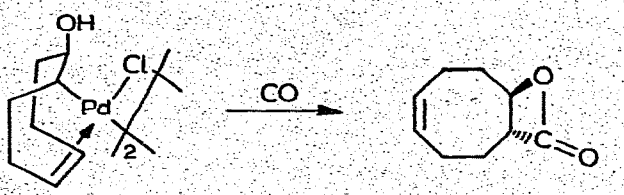
Summary

The reaction of dichloro(1,5-cyclooctadiene)palladium(II) in aqueous sodium carbonate resulted in the formation of the σ-bonded hydroxypalladation enyl complex di-μ-chlorobis(1-hydroxycyclooct-4-ene-8σ,4π)dipalladium(II) (III). Carbonylation of III in water afforded exclusively *trans*-2-hydroxy-5-cyclooctenecarboxylic acid β-lactone IV and demonstrated that hydroxypalladation occurred stereospecifically *trans*.



(III) (IV)

Equimolar quantities of the Wacker oxidation product, 4-cycloocten-1-one, and the palladium hydride addition enyl complex, di-μ-chloro(4-cyclooctene-1σ,4π)-dipalladium(II), were obtained from the reaction of 1,5-cyclooctadiene and water in the presence of palladium chloride.

Introduction

The stereochemical course of the reaction of olefin-transition metal complexes may be considered the result of two distinct mechanistic processes [2]. Reactions in which the addend or nucleophile is coordinated to the metal and trans-

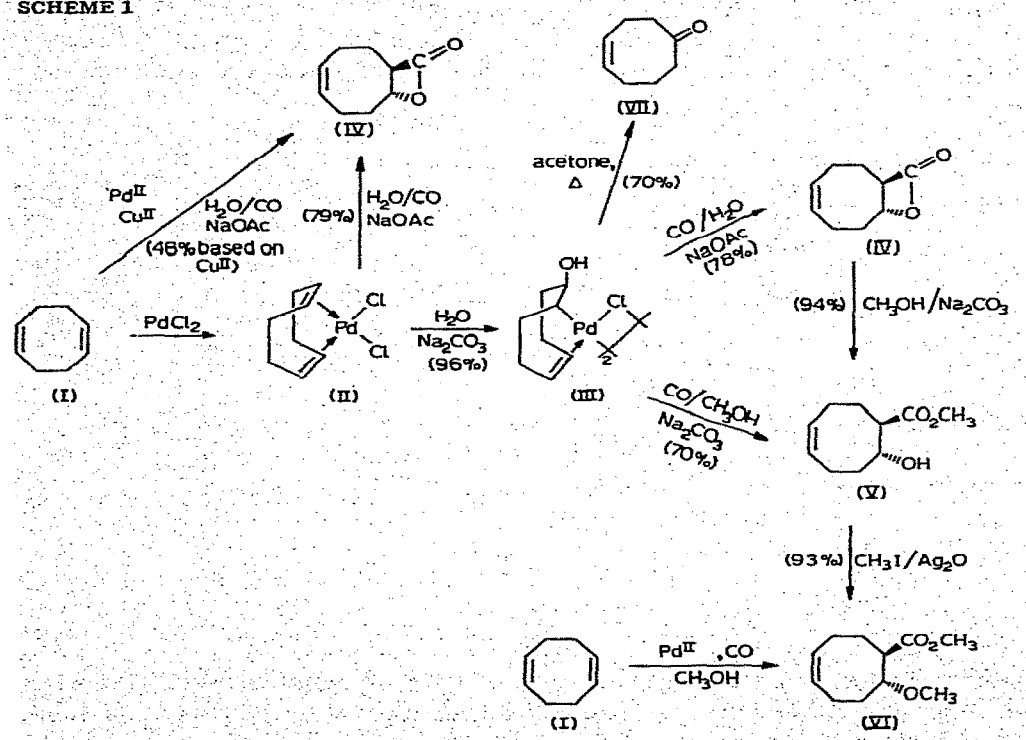
* Abstracted in part from the Ph.D. thesis of D.E. James [1a]; for a preliminary report [1b].

fers directly from the metal to an olefinic carbon proceed by *cis* addition in an anti-Markovnikov direction. Those reactions in which the nucleophile is solvated but not coordinated and forms a bond with an olefinic carbon by external nucleophilic attack proceed by *trans* addition in a Markovnikov direction.

Since the mechanism for the Wacker oxidation [3] of monoolefins was proposed [4] on the basis of kinetic results, to be consistent with *cis* hydroxypalladation in the rate determining step, the stereochemistry of the methoxypalladation of chelating diolefins, which was demonstrated [5,6] to proceed in all cases by direct attack of methanol *exo* on the coordinated double bond of the ligand, was regarded as anomalous [7—11]. However, the analogous *trans* stereochemistry for the methoxypalladation of the monoolefins, *cis*- and *trans*-2-butene, has been established [12].

Clearly, the stereochemistry of the reactions of chelating diolefins can no longer be considered anomalous [13]. *trans* Addition of nucleophiles occurs in the methoxypalladation of both mono- and diolefins as well as in the addition of acetate (monoolefin [14], diolefin [15]) and chloride (monoolefin [16], diolefin [17]). *cis* Phenylpalladation has been demonstrated for both monoolefin [18] and diolefin [19]. Therefore, because of the apparent mechanistic conflict between the course of the oxypalladation reactions of methanol and water, we have investigated the nucleophilic attack by water on coordinated 1,5-cyclooctadiene *.

SCHEME 1



* The preparation of the bromo-bridged dimer, di-μ-bromobis(1-hydroxycyclooct-4-ene-8σ,4π)palladium(II), and some derivatives have been reported but no stereochemical data was included [20].

Results and discussion

The σ-bonded hydroxy enyl complex III was easily prepared by the reaction of water with dichloro(1,5-cyclooctadiene)palladium(II) in the presence of sodium carbonate (Scheme 1). The stereochemistry of the hydroxypalladation reaction was determined by carbon monoxide insertion which has been demonstrated to proceed with 100% retention at the carbon bearing the palladium [15]. Carbonylation of III in water in the presence of sodium acetate afforded metallic palladium and a single organic product, 2-hydroxycyclooct-5-enecarboxylic acid β-lactone (IV), whose structure was assigned from the following evidence. Methanolysis of the lactone in the presence of base yielded exclusively *trans*-methyl 2-hydroxycyclooct-5-enecarboxylate (V) *. Methylation of V gave the *trans* methoxy ester VI as shown by comparison to an authentic sample [15]. Carbonylation of III in methanolic sodium carbonate produced V as the only organic product. β-Lactone IV also can be prepared directly from the diene complex II by carbonylation in aqueous sodium acetate.

In addition, the carbonylation of 1,5-cyclooctadiene (I) employing a catalytic amount of palladium(II) and copper(II) as reoxidant was investigated. A mixture of I, palladium chloride, cupric chloride, and sodium acetate in a water/acetone solution was allowed to react with carbon monoxide (3 atm) at room temperature to afford a 48% yield (based on copper(II)) of IV. In this reaction, 1.7 mmol of palladium(II) gave 11.8 mmol of lactone for a catalytic turnover of 6.9 times.

Thermolysis of III in acetone provided a 70% yield of the γ,δ-unsaturated ketone VII. This is the product expected from the Wacker oxidation of 1,5-cyclooctadiene, a reaction which has been demonstrated to proceed via a σ-bonded β-hydroxyalkylpalladium intermediate [22].

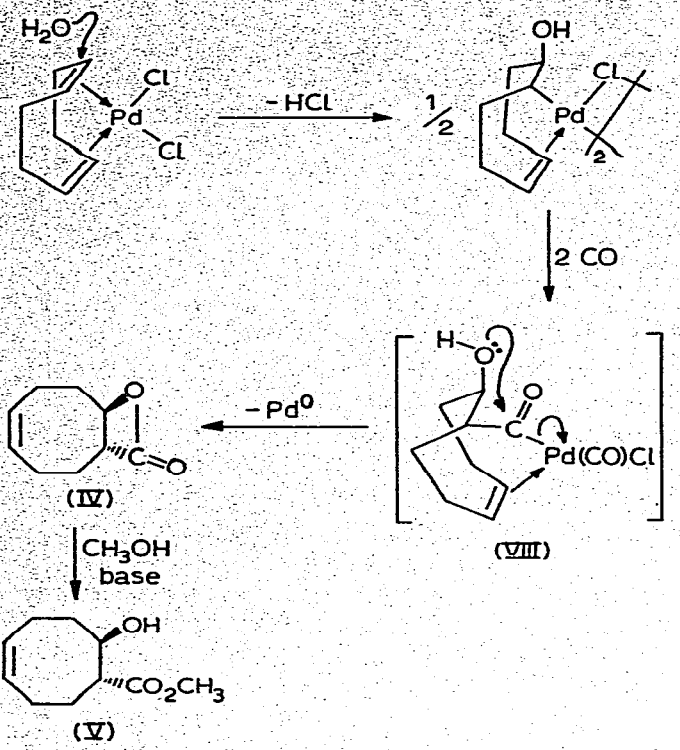
The *trans* stereochemistry of the lactone IV cannot be the result of a base-catalyzed epimerization process. Because of the high reactivity of the strained β-lactone four-membered ring system, any base-catalyzed solvolysis will result in an irreversible ring-opening reaction [21]. Alcoholysis of β-lactones in the presence of a strong base such as alkoxide ion (necessary to cause epimerization at the carbon α to the carbonyl) affords unsaturated esters. Interestingly, treatment of the more stable methoxy ester VI with sodium methoxide in methanol yields predominantly unsaturated ester (70%) [15]. The remainder of the product (30%) is an equimolar mixture of the epimerized *trans*- and *cis*-β-methoxy esters.

The *trans* stereochemistry of the lactone IV, therefore, indicates that as with methanol, oxypalladation proceeds exclusively with attack by the nucleophile (water) from outside the coordination sphere of palladium. The carbonylation reaction mechanism (Scheme 2) probably involves carbon monoxide insertion into the palladium—carbon bond followed by intramolecular alcoholysis of the acylpalladium bond of VIII to give IV. The hydroxy ester V can be formed by base catalyzed methanolysis of IV and/or VIII.

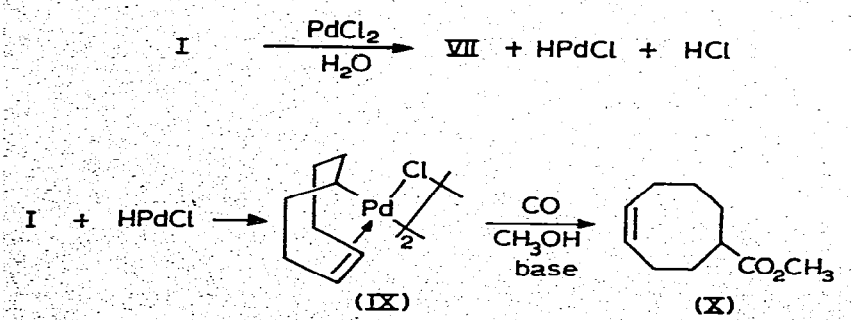
In an attempt to prepare III directly from 1,5-cyclooctadiene [23], a slightly greater than two-fold excess of I was stirred with palladium chloride in water/acetone solution. The reaction resulted in isolation of equimolar amounts of two

* Irreversible heterolysis of the lactone proceeds by acyl—oxygen cleavage, hence the stereochemical integrity of the molecule is maintained [21].

SCHEME 2



SCHEME 3



products, the Wacker oxidation product VII and the dimeric σ-bonded enyl complex IX (Scheme 3). The Wacker oxidation of the diolefin generates Pd(0) and hydrogen chloride (effectively HPdCl) which reacts with another molecule of cyclooctadiene to form the hydride addition complex IX *. Carbonylation of IX yields methyl 4-cyclooctenecarboxylate (X).

* As pointed out by a referee, the formation of IX may be the result of an attack by I on III. Our data cannot distinguish between the two mechanistic possibilities.

Experimental section

Preparation of di-μ-chlorobis(1-hydroxycyclooct-4-ene-8σ,4π)dipalladium(II) (III)

To a stirred solution of 0.50 g (4.7 mmol) of anhydrous sodium bicarbonate in 50 ml of water was added 1.00 g (3.5 mmol) of dichloro(cyclooctadiene)palladium(II) (II) [4]. The reaction was allowed to proceed for 50 min. The cream-colored solid was collected by suction filtration and was washed with methanol, ether, and pentane. The air-dried product was further purified by dissolving it in dichloromethane and reprecipitation by the addition of pentane at −78°C. The product was collected by gravity filtration and air dried to afford 0.88 g (94%) of pale yellow III: m.p. 120°C (dec.), IR (nujol) 3240 cm^{-1} (—OH); ^1H NMR ($CDCl_3$) * δ 6.2—5.3 (m, vinyl), 4.18 (m, H—C—Pd), 3.70 (m, C(2) methyne), 3.4—1.2 (m, methylene) and 1.59 ppm (s, hydroxyl). Anal. Found: C, 36.09; H, 4.85. $C_{16}H_{26}Cl_2O_2Pd_2$ calcd.: C, 35.98; H, 4.91%.

Carbonylation of III in acetone/water in the presence of sodium acetate. Formation of trans-2-hydroxy-5-cyclooctenecarboxylic acid β-lactone (IV)

A mixture of 1.00 g (1.9 mmol) of III, and 0.50 g (6.1 mmol) of anhydrous sodium acetate, 50 ml of acetone, and 2 ml of water were placed in a 250 ml pressure bottle, which was pressurized with 3 atm of carbon monoxide and stirred at room temperature for 4 h. After the reaction, 20 ml of acetone were added, the reaction mixture was filtered, and the black residue was washed with acetone. The acetone filtrates were concentrated under diminished pressure and the residue was extracted with pentane. The pentane extracts were combined, and the solvent removed under reduced pressure to provide 0.45 g (78%) of IV. Final purification of IV was effected by short path distillation under diminished pressure: b.p. 74—75°C/0.18 mmHg; IR (neat) 1829 (strained cyclic ester) and 739 cm^{-1} (*cis*-olefin); ^1H NMR ($CDCl_3$) δ 5.67 (m, 2H, vinyl), 4.36 (m, 1H, C(2) methyne), 3.55 (m, 1H, C(1) methyne) and 2.6—1.0 ppm (m, 8H); ^{13}C NMR ($CDCl_3$) δ 22.12 (methylene), 22.98 (methylene), 24.38 (methylene), 30.85 (methylene), 55.88 (C(1) methyne), 76.76 (C(2) methyne), 129.94 (vinyl), 130.11 (vinyl), and 171.05 ppm (carbonyl), mass spectrum (70 eV) *m/e* 152 ($M^+ - CO_2$). Anal. Found: C, 70.89; H, 7.88. $C_9H_{12}O_2$ calcd.: C, 71.03; H, 7.95%.

Methanolysis of IV in the presence of sodium carbonate. Formation of trans-2-hydroxy-5-cyclooctenecarboxylic acid methyl ester (V)

A solution of 0.7 g (4.6 mmol) of IV in 15 ml of anhydrous methanol containing 0.20 g (19 mmol) of anhydrous sodium carbonate was stirred for 5 h. After the reaction, the methanol was removed under reduced pressure and the residue was extracted with pentane. Evaporation of the solvent under diminished pressure gave 0.80 g (94%) of V. Final purification was effected by preparative VPC using a 20′ × 0.375″ 15% SE 30/Chromosorb W column: IR (neat) 3490 (—OH) and 1740 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 5.62 (m, 2H, vinyl), 3.97 (m, 1H, C(2) methyne), 3.68 (s, 3H, carboxylate methyl), 2.83 (m, 1H, C(1) methyne), 2.6—1.4 (m, 8H), and 2.47 ppm (s, 1H, —OH); ^{13}C NMR ($CDCl_3$) δ 23.52 (meth-

* The solution was insufficiently concentrated to obtain reliable measurements of relative peak areas.

ylene), 24.22 (methylene), 28.48 (methylene), 35.66 (methylene), 50.60 (C(1) methyne), 51.51 (carboxylate methyl), 71.80 (C(2) methyne), 127.84 (vinyl), 130.81 (vinyl), and 176.01 ppm (carbonyl); mass spectrum (70 eV) *m/e* 184 (M^+) and 152 ($M^+ - CH_3OH$). Anal. Found: C, 65.00; H, 9.04. $C_{10}H_{16}O_3$ calcd.: C, 65.19; H, 8.75%.

Methylation of V. Formation of trans-2-methoxy-5-cyclooctenecarboxylic acid methyl ester (VI)

A mixture of 0.82 g (4.5 mmol) of V, 1.62 g (7.0 mmol) of silver oxide, and 1.22 g (9.0 mmol) of anhydrous calcium sulfate in 11.0 g (106 mmol) of methyl iodide were heated at the reflux temperature for 24 h. After reaction, 30 ml of chloroform were added and the mixture was filtered with suction using Celite. The residue was washed with chloroform and the combined extracts were concentrated at diminished pressure to afford 0.87 g (93%) of product. VPC analysis using a 20′ × 0.375″ 15% SE 30/Chromosorb W column showed the presence of two components, unreacted V (5%) and its methylated derivative VI (95%) which was identified by comparison to an authentic sample [15]: ^{1}H NMR ($CDCl_3$) δ 2.5—1.5 (m, 8H), 2.8 (m, 1H, C(1) methyne), 3.28 (s, 3H, methoxyl), 3.5 (m, 1H, C(2) methyne), 3.57 (s, 3H, carboxylate methyl), 5.57 ppm (m, 2H, vinyl).

Carbonylation of III in methanol in the presence of sodium carbonate. Formation of V

To a stirred mixture of 1.00 g (9.5 mmol) of anhydrous sodium carbonate and 50 ml of methanol were added 1.80 g (3.4 mmol) of III and the mixture was allowed to react with carbon monoxide (3 atm) at room temperature for 6 h. After reaction, the mixture was filtered and the residue was washed with methanol. The methanol filtrates were combined and concentrated under reduced pressure and the residue was extracted with pentane. The pentane extracts were combined and the solvent was removed under reduced pressure to provide 0.87 g (70%) of V.

Carbonylation of dichloro(1,5-cyclooctadiene)palladium(II) (II) in water/acetone in the presence of sodium acetate. Formation of IV

To a solution of 2 ml of water and 50 ml of acetone were added 0.50 g (6.1 mmol) of anhydrous sodium acetate and 0.70 g (2.5 mmol) of II and the stirred mixture was allowed to react with carbon monoxide (3 atm) at room temperature for 3 h. Upon completion, the mixture was filtered and the black residue was washed with acetone. The filtrate was then concentrated under diminished pressure and the residue was extracted with pentane. The solvent was removed under reduced pressure to afford 0.30 g (79%) of IV.

Catalytic carbonylation of 1,5-cyclooctadiene (I) in water/acetone. Formation of IV

A mixture of 10 ml of I, 0.31 g (1.7 mmol) of palladium(II) chloride, 6.72 g (50 mmol) of anhydrous cupric chloride, and 8.2 g (100 mmol) of anhydrous sodium acetate in a solution of 3 ml of water and 100 ml of acetone was allowed to react with carbon monoxide (3 atm) for 100 h. After the reaction, the solid

residue was removed by suction filtration and washed with acetone. The filtrate was then concentrated under diminished pressure and the residue was extracted with pentane. The pentane was removed under diminished pressure to afford 4.98 g of product. The crude product was then stirred under reduced pressure (0.25 mmHg) for 30 min at room temperature to remove excess 1,5-cyclooctadiene and afforded 1.79 g (48% based on cupric chloride) of IV.

Thermolysis of III. Formation of 4-cycloocten-1-one (VII)

A solution of 0.40 g (0.75 mmol) of III in acetone was heated at the reflux temperature for 5 h. After reaction, the mixture was concentrated under diminished pressure and the residue was extracted with pentane. The pentane was removed under reduced pressure and 0.13 g (69%) of product identified as 4-cycloocten-1-one [24] was obtained: IR (neat) 1714 (ketone) and 733 cm^{-1} (*cis*-olefins); ^1H NMR ($CDCl_3$) δ 1.59 (m, 2H, C(7) methylene), 2.6—1.9 (m, 8H), and 5.67 ppm (m, 2H, vinyl); mass spectrum (70 eV) *m/e* 124 (M^+).

Preparation of di-μ-chlorobis(4-cyclooctene-1σ,4π)-dipalladium(II) (IX)

To a stirred mixture of 0.18 g (1.0 mmol) of palladium(II) chloride in 10 ml of water and 5 ml of acetone was added 0.25 g (2.3 mmol) of I. After 20 h, the acetone was removed under reduced pressure and the residue was extracted with pentane. The extract was concentrated under diminished pressure to afford 0.12 g (89%) based on palladium(II) of VII which was shown by VPC analysis to contain a trace of I.

The solid residue was next taken up in dichloromethane and was separated from the aqueous layer. The organic layer was dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent gave 0.24 g (96%) based on palladium(II) of IX: ^1H NMR ($CDCl_3$) δ 1.2—0.5 (m, 2H, C(7) methylene), 2.7—1.4 (m, 8H), 3.69 (m, 1H, H—C—Pd), 5.55 (m, 1H, vinyl) and 6.01 ppm (m, 1H, vinyl); ^{13}C NMR ($CDCl_3$) δ 26.24 (methylene), 26.92 (methylene), 28.89 (methylene), 35.54 (methylene), 40.16 (methylene), 57.05 (J(CH) 140.8 Hz, C(1) methyne), 100.95 (J(CH) 159.3 Hz, C(5) vinyl), and 105.43 ppm (J(CH) 155.6 Hz, C(4) vinyl). Anal. Found: C, 38.18; H, 5.02. $C_{18}H_{26}Cl_2Pd_2$ calcd.: C, 38.28; H, 5.22%.

Carbonylation of IX in methanol in the presence of sodium acetate. Formation of 4-cyclooctenecarboxylic acid methyl ester (X)

A stirred mixture of 1.00 g (2.0 mmol) of IX and 0.50 g (6.1 mmol) of anhydrous sodium acetate in 50 ml of methanol was allowed to react with carbon monoxide (3 atm) at room temperature for 4 h. The usual work-up afforded 0.62 g (93%) of X [25]: IR (neat) 1745 cm^{-1} (ester); ^1H NMR ($CDCl_3$) δ 2.7—1.2 (m, 10H), 3.64 (s, 3H, carboxylate methyl), 5.67 ppm (m, 2H, vinyl); mass spectrum (70 eV) *m/e* 168 (M^+), 153 ($M^+ - CH_3$), and 109 ($M^+ - CO_2CH_3$).

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