Journal of Organometallic Chemistry, 169 (1979) 239—248

MECHANISM OF THE WACKER PROCESS. STEREOCHEMISTRY OF THE HYDROXYPALLADATION[1]

J. K. Stille* and R. Divakaruni

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

(Received December 27th, 1978)

SUMMARY

The stereochemistry of hydroxypalladation, the first step in the Wacker oxidation of ethylene to acetaldehyde, was determined using cis-1,2-dideuterio ethylene by intercepting the intermediate β-hydroxyethylpalladium complex with carbon monoxide. The formation of trans-2,3-dideuterio-β-propiolactone from cis-1,2-dideuterioethylene under the Wacker reaction conditions demonstrated that the hydroxypalladation step proceeded stereospecifically trans.

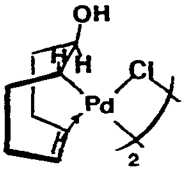
The reaction of propene under the same conditions resulted in the formation of 4-methyl-oxetanone and acetone, demonstrating that the Wacker oxidation and carbonyl insertion were competitive. Other olefins such as butene, and pentene afforded only the ketone oxidation products.

INTRODUCTION

The mechanism of the Wacker oxidation of ethylene to acetaldehyde catalyzed by palladium(II) in aqueous media has been the subject of controversy, particularly with regard to the mechanism of the hydroxypalladation step. Although it is reasonably clear that an unstable β-hydroxyethylpalladium complex is an intermediate, the stereochemistry of its formation and the immediate source of the hydroxyl group, from a position in the complex cis to coordinated ethylene, or external to the complex, is open to question.

The kinetics of the reaction are consistent both with a syn-[2,3] and an anti-hydroxypalladation step. It is generally recognized now, however, that nucleophiles or ligands that are coordinated to palladium, and transfer the group directly from palladium to an olefinic carbon (olefin insertion) proceed by palladium-ligand syn-addition. When this mode of addition takes place, the position of the ligand in the complex relative to the olefin is probably cis.[4] Those nucleophiles that are solvated, but not coordinated to palladium, and form a bond to the olefinic carbon by external nucleophilic attack, undergo reactions by palladium-nucleophile anti-addition.

Anti-addition of hydroxyl and palladium has been shown[5] to take place when the olefin is 1,5-cyclooctadiene, for example, to give the trans palladium complex (1). This stereochemistry of this addition has been considered to be atypical,[6-11] since such a chelating diolefin presents some steric hindrance to syn-addition. More importantly it could not undergo easily the 90° rotation from a position perpendicular to the square plane of the complex into a position in which one of the olefin pair is coplanar with the square plane of the complex, and thus adjacent to a hydroxyl or water ligand, a position necessary for syn-attack.

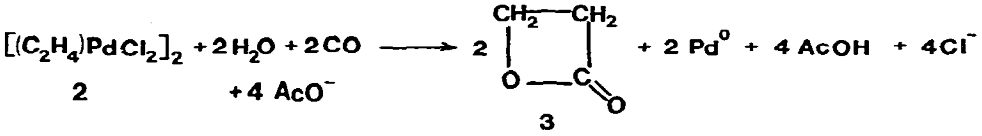


1

RESULTS AND DISCUSSION

In order to establish the stereochemistry of the Wacker oxidation of ethylene, the hydroxypalladation of cis-12,-dideuterioethylene was undertaken under conditions similar to the Wacker reaction. The trapping of the intermediate unstable β-hydroxyethylpalladium complex was effected with carbon monoxide.

The reaction of bis-benzonitrile palladium(II) chloride with ethylene results in the formation of the ethylene palladium chloride complex (2). When this complex reacted with carbon monoxide in aqueous acetonitrile containing sodium acetate as a buffer at -20 to -25°, β-propiolactone (3) was formed in 64% conversion.



The direct catalytic conversion of ethylene to 3 could be effected from a 2:1 ethylene:carbon monoxide charge (total 3 atm) in aqueous acetonitrile using catalytic amounts of palladium(II) chloride, equivalent amounts of copper(II) chloride as a reoxidant, and sodium acetate as a buffer at -20 to -25° (Table I). No acetaldehyde by-product could be detected in the reaction product mixture. Since copper(I) can be reoxidized to copper(II) by air, this represents a unique catalytic synthesis of β-lactones from olefin, carbon monoxide, and air.

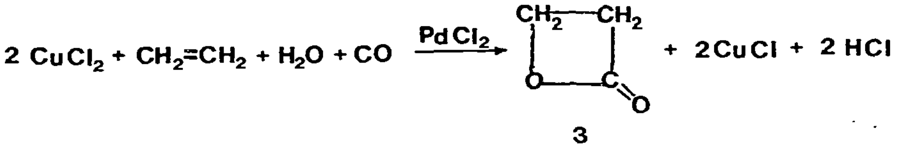


TABLE I

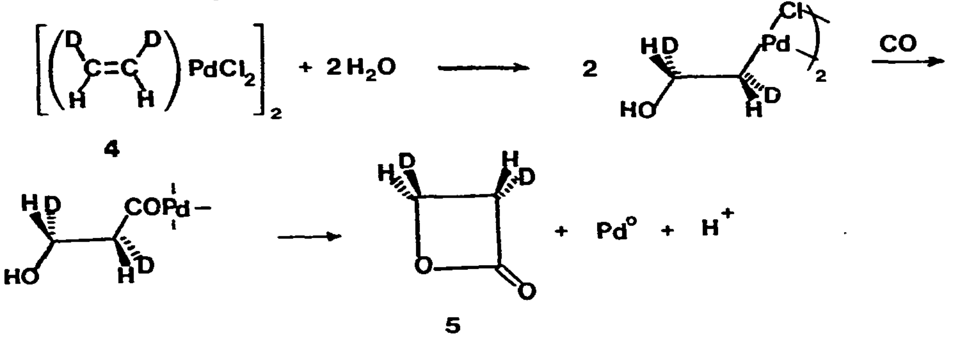
Catalytic Carbonylation of Ethylene to β-Propiolactone[a]

Catalyst	Temp°C	Conversion to 3(%)
PdCl$_2$,(PhCN)$_2$PdCl$_2$, or [C$_2$H$_4$PdCl$_2$]$_2$	25°	0
[C$_2$H$_4$PdCl$_2$]$_2$	-20 to -25°	39°
PdCl$_2$	-20 to -25°	37%

---

[a] The carbon monoxide ethylene charge was 1:2 (total 3 atm).

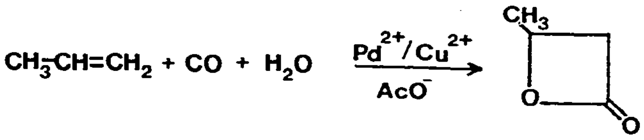
The stereochemistry of the hydroxypalladation step was determined by using the ethylene palladium(II) chloride complex (4) obtained from cis-1,2-dideuterioethylene.[13] The reaction of 4 with carbon monoxide in aqueous acetonitrile using sodium acetate as buffer afforded trans-2,3-dideuterio-propiolactone (5).



The stereochemistry for the lactone (5) was assigned trans on the basis of the proton coupling constants. The calculated coupling constants for the two protons H_a and H_b using the Karplus equation[4] are 7.2Hz for the cis isomer and 3.7Hz for the trans isomer. The coupling constants reported for 2,3-diphenylpropiolactone[15] are 7.0Hz for the cis isomer and 4.5Hz for the trans isomer; the coupling constant observed for lactone 5 was 4.0Hz.

Since the insertion of carbon monoxide into a carbon-palladium sigma-bond occurs with retention of configuration at carbon,[13] the hydroxy-palladation step in this reaction, and presumedly in the Wacker reaction, must proceed with anti-stereochemistry. This implies that the hydroxylation takes place from outside the coordination sphere of palladium; the cis arrangement of olefin and hydroxyl or water in the complex is not necessary. These results for the stereochemistry of hydroxypalladation are consistent with those reported[16] for the reaction of trans-1,2-dideuterio-ethylene under the conditions of the Wacker reaction. The formation of threo-1,2-dideuterio-2-chloroethanol also requires anti hydroxypalladation.

The direct catalytic conversion of propylene to 4-methyloxetanone (3-methyl-β-propiolactone) (6) in 17-18% conversion could be effected from a 2:1 propylene/carbon monoxide charge using catalytic amounts of palladium(II) and equivalent amounts of copper(II) chloride.



6

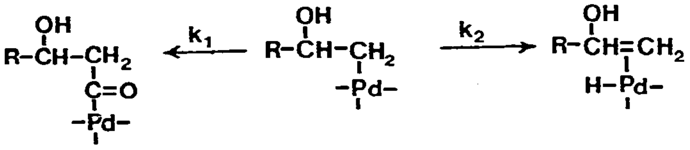
As in the case of ethylene, the reaction took place readily only at lower temperatures. A 30% conversion of propylene to 6 was effected using stoichiometric amounts of palladium(II) chloride. The propylene(II) palladium chloride complex could not be isolated, but a significant amount of the Wacker oxidation product, acetone, was formed in these reactions (Table II). Thus, the oxidation and the carbonylation of the intermediate β-hydropalladium complex are competitive even at low temperatures. The carbonylation of terminal olefins other than ethylene and propylene in aqueous acetonitrile at -20 to -25° resulted only in the formation of the ketone oxidation products. In the case of 1-butene and other higher terminal olefins, the rate of decomposition to oxidation products, is competitive, since palladium hydride elimination is fastest when the hydride is on a 3° carbon,[17] particularly one bearing a hydroxyl function ($k_2 >> k_1$).

TABLE II

Catalytic Carbonylation of Propylene to 4-Methyloxetanone[a]

			%	
Mmole $CuCl_2$	Mmole NaOAc	Mmole H_2O	Conversion to Lactone	to Acetone
50	50	50	18	59
100	100	50	17	53
50	50	100	18	62

[a] Carbon monoxide:propylene charge was 1:2.

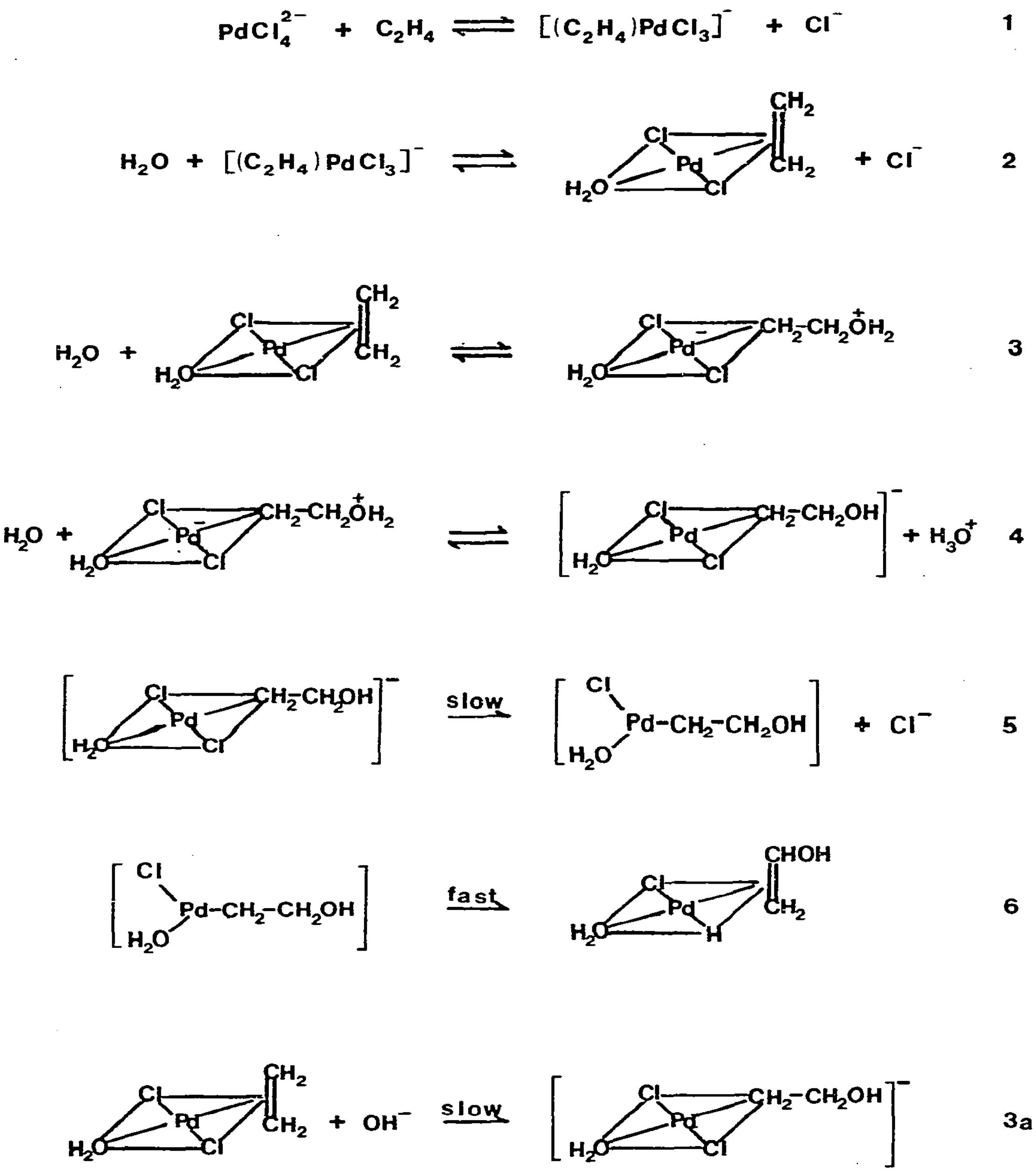


$R = H, \ k_1 > k_2$

$CH_3, \ k_1 \simeq k_2$

$C_2H_5, \ k_1 < k_2$

Scheme I


PdCl4 2− + C2H4 ⇌ [(C2H4)PdCl3]− + Cl−
1
H2O + [(C2H4)PdCl3]− ⇌
Cl Pd H2O Cl CH2 CH2
+ Cl−
2
H2O +
CH2-CH2OH2+
3
H2O + H3O+
CH2-CH2OH
4
slow
Pd-CH2-CH2OH
+ Cl−
5
fast
CHOH
CH2
H
6
+ OH−
slow
3a

Although the kinetics of the oxidation of ethylene are complex,[2,18] the anti-hydroxypalladation mechanism, in which the hydroxyl or water comes from outside the coordination sphere, must also be consistent with the rate data. In particular, a mechanism which is first order in ethylene and $PdCl_4^{2-}$, inverse order in hydrogen ion concentration, and at least inverse second order in chloride ion, is required. The mechanisms shown are consistent with these data, and also the stereochemistry (Scheme I). Either the rate determining step is the dissociation of chloride (eq. 5) which has been preceeded by attack of water on the olefin complex (eq. 3), or the rate determining step is the attack of hydroxide on the olefin complex (eq. 3a).

EXPERIMENTAL

Carbonylation of ethylene palladium(II) chloride (2). Formation of β-propiolactone (3).

A solution of 2.20 g (5.36 mmol) of ethylene palladium(II) chloride (2)[12] in 50 ml of acetonitrile was treated with 4.00 g (48.8 mmol) of anhydrous sodium acetate and 0.90 g (50.0 mmol) of water. The mixture was cooled with stirring to -20 to -25°C (Dry-Ice/carbon tetrachloride bath). The reaction mixture was pressurized with 3 atm of carbon monoxide for 9 hr at the end of which time the solution turned black and no more carbon monoxide uptake was noticed. The acetonitrile was distilled using a Vigreux column.

Vpc analysis of the oily liquid showed the presence of one product in 64% conversion identified as β-propiolactone (3) by comparison with an authentic sample.[19] Ir (neat) 1820 cm^{-1} (lactone carbonyl). ^1H nmr ($CDCl_3$) δ 3.9 (m, 2H, C-3 methylene), 3.2 (m, 2H, C-2 methylene). ^{13}C nmr (neat) δ 165.59 (carbonyl), 57.63 (C-3, methylene), 38.40 (C-2 methylene). Mass spectrum (70 eV) m/e (relative intensity) 72 (M^+, 33), 44 (CO_2^+, 28), 42 (M^+-CH_2O, 54), 30 ($M^+-C_2H_2O$, 90), 28 (M^+-CO_2,100). Anal. Calcd for $C_3H_4O_2$: C, 50.00; H, 5.60. Found: C, 49.71, H, 5.74.

Catalytic carbonylation of ethylene. Formation of 3

A suspension of 13.44 g (100.0 mmol) of copper(II) chloride and 8.00 g (97.6 mmol) of anhydrous sodium acetate in 75 ml of dry acetonitrile was treated with 0.90 g (50.0 mmol) of water and 0.50 g (2.80 mmol) of palladium(II) chloride. The mixture was cooled to -20 to -25°, and the system was then subjected to 1 atm of ethylene, and the pressure was increased to 3 atm with carbon monoxide. As the pressure of the system decreased, more carbon monoxide was introduced into the system. After 48 hr, no more uptake was observed.

The reaction mixture was cooled in an ice bath and the contents of the vessel were carefully transferred to a fractional distillation apparatus. The acetonitrile was distilled and collected in seven 8 ml fractions. Each of these fractions was treated with a solution of 0.2 g of 2,4-dinitrophenyl hydrazine in 4 ml of methanol. No precipitation was observed in any of th fractions indicating the absence of acetaldehyde in the reaction mixture.

The residual mixture was worked up as before; vpc analysis showed the formation of (3) in 39% conversion.

Preparation of cis-1,2-dideuterioethylenepalladium(II) chlorides, (4)

Cis-1,2-dideuterioethylene was prepared as described.[10] The mass spectrum indicated that contamination by undeuterated or monodeuterated ethylene was less than 5%. The cis-1,2-dideuterioethylene was condensed into a liquid nitrogen trap, and then the trap was removed in order to allow the gas to bubble slowly into a solution of 10.00g (26.04 mmol) of bis-benzonitrile palladium(II) chloride in 120 ml of benzene. The cis-1,2-dideuterioethylene was bubbled until the precipitation of the ethylene complex was complete. The yellow solid was filtered, and washed with petroleum ether to yield 5.02 g (93%) of the dideuterioethylenepalladium(II) chloride (4).

Carbonylation of (4). Formation of trans-2,3-dideuteriopropiolactone (5)

A solution of 4.72 g (11.4 mmol) of 4 in 50 ml of acetonitrile was treated with 4.00 g (48.8 mmol) of anhydrous sodium acetate and 0.90 g

(50.0 mmol) of water. The mixture was cooled to -20 to -25° and subjected to 3 atm of carbon monoxide. After 10 hr, no more carbon monoxide uptake was observed. The acetonitrile was distilled using a Vigreux column. Analysis of the residual liquid on vpc indicated the formation of trans-2,3-dideuteriopropiolactone (**5**). The product was identified by the ^1H nmr coupling constants[14] and by comparison with the coupling constants reported for other substituted β-propiolactones.[15] Ir 1820 cm^{-1} (lactone carbonyl). ^1H nmr ($CDCl_3$) 4.2 (1H, d, J=4 Hz), 3.2 (1H, d, J=4 Hz).

Catalytic Carbonylation of Propylene. Formation of 4-Methyloxetanone (3-methyl-propiolactone) (**6**)

A solution of 13.44 g (100.0 mmol) of cupric chloride in 75 ml of acetonitrile was treated with 8.00 g (97.6 mmol) of sodium acetate, 0.90 g (50.0 mmol) of water and 0.50 g (2.8 mmol) of palladium(II) chloride. The mixture was cooled with stirring to -20 to 25° and subjected to 1 atm of propylene. The total pressure was increased to 3 atm with carbon monoxide. As the pressure of the system decreased, more carbon monoxide was introduced into the reaction vessel. After 38 hr, no further uptake was observed.

The reaction mixture was slowly allowed to warm to 0°C. Vpc analysis of the FFAP column indicated the formation of two products, acetone, and **6** in varying yields (Table II). The identity of acetone was proved by ^1H nmr analysis and conversion to the 2,4-dinitro phenyl hydrazone; m. p. 158° (Lit.[20]= 158-159°).

The other product was determined to be a four-membered lactone, identified as **6** (17%) by spectral analysis[21] and by an independent synthesis from crotonic acid.[22] Ir (neat 1830 cm^{-1} (lactone carbonyl). ^1H nmr ($CDCl_3$) δ 4.5-5.8 (1H, methyne), 3.5-3.6 (1H, methylene, H trans to methylene H), 2.8-2.9 (1H, methylene H, cis to methyne H). 1.6 (d, 3H, methyl). ^{13}C nmr 168.73 (carbonyl), 53.25 (C-2), 43.50 (C-3), 20.00 (CH_3). Mass spectrum (70 eV m/e (relative intensity) 86 (M^+, 12), 73 (M^+ $-CH_3$, 100), 44 (M^+ $-C_2H_2O$, 34), 42 (M^+ $-CH_3CHO$ or CO_2, 85), 15 (CH_3^+, 10). Anal. Calcd for $C_4H_5O_2$: C, 55.80; H, 7.03; Found: C, 55.31; H, 6.98.

This research was supported by the National Science Foundation, Grant CHE 77-08349.

REFERENCES

1. A preliminary account of this work has appeared: J. K. Stille and R. Divakaruni, J. Am. Chem. Soc., 100, 1303 (1978).
2. P. M. Henry, Accts. Chem. Res., 6, 16 (1973); J. Am. Chem. Soc., 86, 3246 (1964); ibid., 88, 1595 (1966); Adv. Organometal. Chem., 13, 363 (1975).
3. P. M. Matlis, The Organic Chemistry of Palladium VII, Academic Press, New York, 1971, p. 82.
4. A. W. Parkins and R. C. Slade, Nature, 256, 635 (1975).
5. J. K. Stille and D. E. James, J. Organometal. Chem., 108, 401 (1976).
6. P. M. Henry, Adv. Chem. Ser., No 70, 151 (1968); Div. Pet. Chem. Prepr., Am. Chem. Soc., 14, F17 (1969).
7. R. F. Heck, Fortschr. Chem. Forsch, 16, 221 (1971).
8. M. Green and R. F. Hancock, J. Chem. Soc. A, 2054 (1967).
9. B. L. Shaw, Chem. Comm., 464 (1968), Div. Pet. Chem., Prepr., Am. Chem. Soc., 14, F17 (1969).
10. F. R. Hartley, Nature (London), 223, 615 (1969).
11. C. Burgess, F. R. Hartley, and G. W. Searle, J. Organomet. Chem., 76, 247 (1974).
12. M. S. Kharasch, R. C. Seyler and W. Frank, J. Am. Chem. Soc., 60, 382 (1938).
13. P. O. Nicholas and R. T. Caroll, J. Org. Chem., 33, 2345 (1968).
14. M. Karplus, J. Am. Chem. Soc., 85, 2870 (1963).
15. O. L. Chapman and W. R. Adams, J. Am. Chem. Soc., 90, 2333 (1968).
16. J. E. Bäckvall, B. Åkermark, and S. O. Ljunggren, J. Chem. Soc., Chem. Comm., 264 (1977).
17. L. F. Hines and J. K. Stille, J. Am. Chem. Soc., 94, 485 (1972).
18. I. I. Moiseev, O. G. Leranda, and M. N. Vargaftik, J. Am. Chem. Soc., 96, 1003 (1974). and references cited therein.
19. Kh. Z. Kotovich, T. V. Vasilina, E. N. Mokryi, D. K. Tolopko, M. D. Fedevich, and I. I. Yatchishin, Visn. L'viv. Polytekh. Inst., 58, 30 (1972).
20. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., New York, 1956.
21. L. Birkofer, A. Ritter and J. Schramm, Chem. Ber., 95, 426 (1962).
22. I. L. Finar, "Organic Chemistry Fundimental Principles", Vol. 1, Longman Greens Ltd., 1967, p. 428.