2938 © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *59*, *2938—2940 (1986)* [Vol. 59, No. 9

A Consideration on the Mechanism of the Wacker Reaction from the Viewpoint of the Trans Influence of Ligands ($OH^- > Cl^- > H_2O$)

Sumio Shinoda, Yasuyuki Koie, and Yasukazu Saito*
Institute of Industrial Science, The University of Tokyo,
22-1, Roppongi 7 Chome, Minato-ku, Tokyo 106

(Received February 22, 1986)

Synopsis. The trans influence of three ligands (OH^-, Cl^-, and H_2O) was compared for the first time according to the same experimental standard ($^1J(PtP_{trans})$). Based on the extremely high trans influence of the OH^- ligand, a mechanism was proposed for the palladium(II) oxidation of ethylene, which includes the rate-determining external attack of H_2O on a possible intermediate, *trans*-$[PdCl_2(OH)(C_2H_4)]^-$.

Although the palladium(II) oxidation of ethylene (the Wacker reaction) has been studied extensively, its mechanistic details (the stereochemistry of the hydroxypalladation and the nature of the rate-determining step) are still the subject of some debate.[1,2] While the mechanism proposed by Henry (rate-determining *syn*-hydroxypalladation) is consistent with the kinetics,[1] Bäckvall et al.[3] proposed a mechanism of the Wacker reaction which reconciles the anti stereochemistry of the hydroxpalladation step with the kinetics. The important point is that the hydroxylation occurs in a *reversible* reaction by the external attack of water on $[PdCl_2(OH_2)(C_2H_4)]$ (Eq. 1), followed by a rate-determining step in which the loss of chloride ion from $[HOCH_2CH_2PdCl_2(OH_2)]^-$ (Eq. 2) takes place.

$$[PdCl_2(OH_2)(C_2H_4)] + H_2O \rightleftarrows [HOCH_2CH_2PdCl_2(OH_2)]^- + H^+ \tag{1}$$

$$[HOCH_2CH_2PdCl_2(OH_2)]^- \rightleftarrows [HOCH_2CH_2PdCl(OH_2)] + Cl^- \tag{2}$$

However, the reversibility of Eq. 1 was seriously questioned on the basis of the deuterium isotope effect for ethylene-1,1-d_2,[4] and later on the basis of the relative rate of isomerization vs. oxidation with allyl-1,1-d_2 alcohol adopted as a substrate (very slow isomerization via hydroxypalladation-deoxypalladation processes, despite the rate expression for oxidation being the same as that for ethylene oxidation).[5,6] Thus, if anti stereochemistry is assumed for the hydroxypalladation step, the most likely mechanism which is consistent with the kinetics would be a rate-determining attack of H_2O on a $[PdCl_2(OH)(C_2H_4)]^-$ species.[7] In the present paper, we would like to discuss the possibility of this mechanism from the points of view of (i) the activation of coordinated ethylene toward the external attack of an H_2O molecule, (ii) the nature of the ethylene–palladium(II) bond, and (iii) the trans influence of the OH^- ligand. Some of the experimental data are our own and are presented here for the first time.

In a previous paper,[4] we suggested that the displacement of the coordinated ethylene to an unsymmetrical position was important in the Wacker reaction; its transition-state structure contrasts with that of ethylene methoxy-mercuration, which is accompanied by considerable C–O bond formation.[10] Actually, Eisenstein and Hoffmann[11] showed that a symmetrically η^2-coordinated olefin was deactivated toward attack by an external nucleophile, and that olefin slipping, a deformation to η^1 coordinantion, played a crucial role in activating the olefin, with an increase in the overlap population between the π^* orbital of the olefin and the electron pair of the nucleophiles. This idea was supported by recent experimental findings.[12]

The bonding nature of metal-ethylene π-complexes $[MCl_3(C_2H_4)]^-$ (M=Pd, Pt) was investigated by means of ab initio calculations on an extended basis,[13] where the creditability of the calculations was ensured by the agreement between the calculated and observed values for both the geometry and the barrier to rotaion in $[PtCl_3(C_2H_4)]^-$. For this complex, the amounts of σ-donation and π-back-donation were evaluated as 0.24 and 0.22 electrons respectively. As for $[PdCl_3(C_2H_4)]^-$ the corresponding values are 0.12 (σ-donation) and 0.07 (π-back-donation) electrons, indicating the weakness of the Pd-ethylene bond relative to the Pt-ethylene bond. By comparing these two values ($0.12 > 0.07$), it was also concluded that σ-donation is more important than π-back-donation in the case of $[PdCl_3(C_2H_4)]^-$. In fact, many kinds of experiments support these trends.[14–16]

Previously, an unexpectedly high trans influence of the OH^- ligand in comparison with the Cl^- ligand was pointed out[4] on the ground of the $^1J_{PtP}$ values for the Pt(II) complexes $[PtX(CH_3)(Ph_2PCH_2CH_2PPh_2)]$.[17] We determined here the corresponding value for the aqua complex, together with the acetone complex (Table 1), to complete the comparison of the trans influence among OH^-, Cl^-, and H_2O ligands. Table 1 unequivocally confirms that the trans influence of

Table 1. $^{195}Pt-^{31}P$ Nuclear Spin Coupling Constants of $[PtX(CH_3)(dppe)]$ Complexes ($dppe = Ph_2PCH_2CH_2PPh_2$)[a)]

Complex	J_{PtP} (trans to X)	J_{PtP} (trans to CH_3)
	Hz	Hz
$[Pt(H_2O)(CH_3)(dppe)]BF_4$[b)]	4722	1821
$[Pt(Me_2CO)(CH_3)(dppe)]BF_4$[b)]	4619	1821
$[Pt(Cl)(CH_3)(dppe)]$	4255 (4224)	1729 (1737)
$[Pt(OH)(CH_3)(dppe)]$	3474 (3546)	1829 (1804)

a) Measured at 30 °C in CH_2Cl_2 (0.3 mol dm^{-3}; JEOL FX-60Q, 24.20 MHz). Data in parentheses are from Ref. 17. b) Prepared according to the literature methods.[17,28)]

Table 2. Some Characteristics of OH^-, Cl^-, and H_2O Ligands

Ligand	P_L/V[a]	*trans*-$[ML(CO)(PPh_3)_2]$ (M=Rh, Ir) ν_{CO}/cm^{-1} [b] Rh	ν_{CO}/cm^{-1} [b] Ir	$E_{1/2}^{ox}$/V[c] Rh	$E_{1/2}^{ox}$/V[c] Ir	E_{homo}/a.u.[d]
OH^-	−1.55	1961	1949	−2.45	−2.68	−0.0941
Cl^-	−1.19	1980	1965	−2.05	−2.22	
H_2O						−0.7121

a) $P_L = E_{1/2}^{ox}[Cr(CO)_5L] - E_{1/2}^{ox}[Cr(CO)_6]$. From Ref. 29. b) From Ref. 30. c) Standard: Ag/Ag$^+$ 0.1 mol dm^{-3} CH_3CN solution. From Ref. 31. d) From Ref. 20.

OH^- is far stronger than not only Cl^- but also H_2O. Since the $^1J_{PtP}$ value reflects well the σ-bond strength between the platinum and phosphorus atoms, [18] it can be said that the Pt-P(trans) σ bond is most weakened in the case of the hydroxo complex because of the strongest σ bonding between the platinum(II) and the OH^- ligand.[19]

As far as we know, there are no other data available for comparing these three ligands on the same experimental standard . However, some relevant data are collected in Table 2. It is obvious from Table 2 that OH^- is the most electron-donating among the three. With respect to theoretical studies, the CNDO/2 calculations of pentaammine complexes $[M(NH_3)_5X]$ ($M=Co^{2+}$, Co^{3+}, Fe^{2+}, and Fe^{3+}; X=FH, OH_2, CO, NH_3, pyridine, OH^-, F^-, and CN^-) showed that the M-NH_3 bond was weakened when the trans ligand was changed from H_2O to OH^-.[20] Recently, on the basis of the equilibrium geometry obtained by ab initio calculations with energy-gradient methods, the trans influene order of $OH^- > Cl^- > NH_3 > H_2O$ was concluded.[21]

According to the analysis of the palladium(II)-ethylene bond (vide supra), σ-donation (from the ethylene π orbital to the Pd d_σ orbital) is important. Taking into consideration the strong trans influence of the OH^- ligand (relative to Cl^- and H_2O), it is quite conceivable that the η^2-coordinated ethylene slips most easily when its trans position is occupied by this ligand.[22] If this process occurs exclusively for the hydroxo complex, the observed kinetics is compatible with the anti stereochemistry of hydroxy-palladation.

References

1) P. M. Henry, "Palladium Catalyzed Oxidation of Hydrocarbons," Reidel, New York (1980), Chap. 2.

2) H. E. Bryndza, *Organometallics*, **4**. 406 (1985), and the references cited therein.

3) J. E. Bäckvall, B. Åkermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, **101**, 2411 (1979).

4) Y. Saito and S. Shinoda, *J. Mol. Catal.*, **9**, 461 (1980); M. Kosaki, M. Isemura, Y. Kitaura, S. Shinoda, and Y. Saito, *J. Mol. Catal.*, **2**, 351 (1977).

5) W. K. Wan, K. Zaw, and P. M. Henry, *J. Mol. Catal.*, **16**, 81 (1982).

6) N. Gregor, K. Zaw, and P. M. Henry, *Organometallics,*, **3**, 1251 (1984).

7) Bäckvall et al.[3] and Henry et al.[5] noted that the nucleophilic attack on a negatively charged π-olefin-metal complex is unlikely. However, even if this reaction is supposed to be driven by a cationic charge on the coordinating carbon atom, its charge density would not necessarily be determined by the formal charge of the complexed ion as a whole. Rather, the trans influence of ligands,[8] either ionic or neutral, seems more important. For instance, the ^1H chemilcal shifts and ν(Ir-H) of a series of hydridoiridium(III) complexes *trans*-$[H(L)Ir(CO)(Cl)(PPh_3)_2]$ were shown to be understandable in terms of the σ-donor strength of the trans ligand L,[9] quite independent of the formal charge of the complex.

8) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

9) B. Olgemöller and W. Beck, *Inorg. Chem.*, **22**, 997 (1983).

10) S. Shinoda, M. Isemura, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **52**, 1855 (1979).

11) O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, **103**, 4308 (1981); **102**, 6148 (1980).

12) L. Maresca and G. Natile, *J. Chem. Soc., Chem. Commun.*, **1983**, 40.

13) P. J. Hay, *J. Am. Chem. Soc.*, **103**, 1390 (1981).

14) D. W. Wertz and M. A. Moseley, *Inorg. Chem.*, **19**, 705 (1981); *Spectrochim. Acta A*, **36A**, 467 (1980).

15) H. Kurosawa, T. Majima, and N. Asada, *J. Am. Chem. Soc.*, **102**, 6996 (1980).

16) W. Partenheimer, *J. Am. Chem. Sco.*, **98**, 2779 (1976).

17) T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, **17**, 738 (1978).

18) Y. Koie, S. Shinoda, and Y. Saito, *Inorg. Chem.*, **20**, 4408 (1981).

19) E. J. Shustrovich, *J. Am. Chem. Soc.*, **100**, 7513 (1978).

20) E. Kai, T. Misawa, and K. Nishimoto, *Bull. Chem. Soc. Jpn.*, **53**, 2481 (1980).

21) H. Basch, M. Krauss, W. J. Stevens, and D. Cohen, *Inorg. Chem.*, **24**, 3313 (1985).

22) Due to the strong trans influence of ethylene, the formation of *trans*-$[PdCl_2(H_2O)(C_2H_4)]$ is substantial.[1] It is well known that the proton-dissociating ability of H_2O is enhanced by coordination with metal ions.[23] Further, this effect is emphasized when there is an olefin ligand at its trans position.[24] Leden and Chatt estimated the acid-dissociation constant of $[PtCl_2(H_2O)(C_2H_4)]$ to be of the order 10^{-5},[25] while Henry assumed 10^{-6} as the corresponding value of $[PdCl_2(H_2O)(C_2H_4)]$.[26] Although he claimed the presence of kinetically significant amounts of the intermediate *cis*-$[PdCl_2(OH)(C_2H_4)]^-$ on this standard (also assuming about 10% *cis*-form in the total), the acid-dissociation constant may be much higher in view of the extremely high affinity of Pd(II) to OH^- in comparison with Pt(II) (Eqs. 3 and 4).[27]

$$[PdCl_4]^{2-} + OH^- \rightleftharpoons [PdCl_3(OH)]^{2-} + Cl^-, \quad \log_{10} K = 5.7 \ (\mu = 1.0,\ 19\text{—}50\ ^\circ C) \tag{3}$$

$$[PtCl_3(OH)]^{2-} + Cl^- \rightleftharpoons [PtCl_4]^{2-} + OH^-, \quad \log_{10} K = 8.66 \ (\mu = 1.0,\ 25\ ^\circ C) \tag{4}$$

23) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962); M. I. Gel'fman, *Koord. Khim.*, **2**, 1369 (1976).

24) Yu. N. Kukushkin, K. M. Trusova, V. F. Budanova, and G. N. Sedova, *Koord. Khim.*, **4**, 436 (1978).

25) I. Leden and J. Chatt, *J. Chem. Soc.*, **1955**, 2936.

26) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

27) F. R. Hartley, "The Chemistry of Platinum and Palladium," Applied Science Publishers, London (1973), pp. 237—238.

28) D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, **199**, 119 (1980).

29) J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, **1980**, 2032.

30) L. Vaska and J. Peone, Jr., *Chem. Commun.*, **1971**, 418.

31) G. Schiavon, S. Zecchin, and G. Pilloni, *J. Inorg. Nucl. Chem.*, **39**, 115 (1977).