Rates and Mechanism of the Reversible Oxidative Addition of (*Z*)- and (*E*)-1,2-Dichloroethylene to Low-Ligated Zerovalent Palladium[†]

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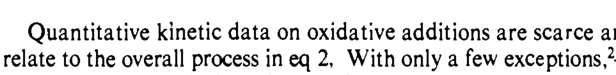
Abstract: Electrochemical reduction of $Pd^{II}Cl_2(PPh_3)_2$ affords a low-ligated zerovalent palladium complex which is shown to undergo a facile oxidative addition by (*Z*)- or (*E*)-1,2-dichloroethylene. In each case, the reaction is shown to proceed rapidly and quantitatively to the corresponding *cis*-σ-vinylpalladium(II) complex. The formation of the cis intermediate occurs via two reversible steps: (i) a rapid and exergonic coordination of the dihaloalkene to the low-ligated palladium(0) is followed by (ii) an inner-shell oxidative addition step. For the *E* isomer an additional step then involves the reversible and exergonic coordination of a second molecule of dichloroethylene to the *cis*-σ-vinylpalladium(II) complex. On a much longer time scale, the *cis*-σ-vinylpalladium(II) complexes isomerize to the more stable *trans*-σ-vinylpalladium(II) ones. The consequences of the rates and of the reversibility of the overall oxidative addition process for palladium-catalyzed nucleophilic substitutions or cross-coupling reactions involving carbon–halogen vinylic bonds are discussed.

Introduction

The palladium complex catalysis of cross-coupling reactions is a well-established method in organic synthesis.[1] Among these the stereospecific palladium-catalyzed substitution of vinyl halides is a convenient way to achieve difficult nucleophilic substitutions at an sp^2 carbon center.[1-3] The reaction is thought to proceed through a succession of three basic steps as summarized in Scheme I:[1,4] (i) oxidative addition of the alkenyl halide to a palladium(0) complex; (ii) substitution at the palladium center of the halide ion by the nucleophilic moiety; (iii) reductive elimination of the substituted olefin and regeneration of the zerovalent palladium complex.

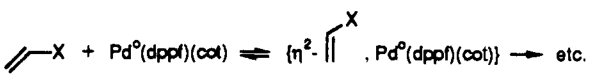
The zerovalent palladium catalyst used in Scheme I may be a chemically stable complex, Pd^0L_4, such as tetrakis(triphenylphosphine)palladium.[5] Alternatively, a low-ligated zerovalent palladium formed in situ,[4g,6] possibly by homogeneous reduction of a divalent precursor,[6] can be used. Despite the large number of synthetic reactions based upon such processes, only limited information is available on the mechanism of this specific class of oxidative additions.[7] It is usually considered that the reaction proceeds in several[4g,8,9] steps to afford the thermodynamically stable[4b,8] *trans*-σ-vinylpalladium(II) complex, presumably via the intermediacy of a *cis*-σ-vinylpalladium(II) species:[8a,c,d]

$$Pd^{II}L_2X_2 \xrightarrow{\text{redn}} Pd^0L_2 + 2X^- \qquad (1)$$



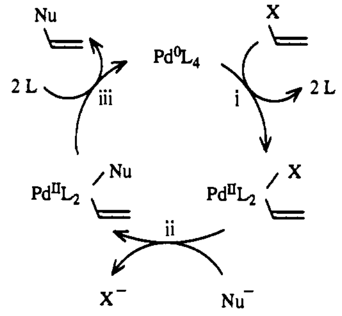
$$\text{CH}_2{=}\text{CH}{-}X + Pd^0L_n \xrightarrow{-(n-2)L} \cdots \rightarrow \text{CH}_2{=}\text{CH}{-}\overset{L}{\underset{X}{Pd^{II}}}{-}L \rightarrow \text{CH}_2{=}\text{CH}{-}\overset{L}{\underset{L}{Pd^{II}}}{-}X \qquad (2)$$

Quantitative kinetic data on oxidative additions are scarce and relate to the overall process in eq 2. With only a few exceptions,[2j,4g] proper kinetic resolution of each of the above steps has not been achieved. In fact the reaction may be more complex than suggested by eq 2. Indeed, it has been shown recently on the basis of an NMR structural study[4g,9] that for the case of poorly ligated zerovalent palladium complexes such as Pd(dppf)(cot) [dppf = 1,1′-bis(diphenylphosphino)ferrocene, cot = cyclooctatetraene] the reaction may involve a rapid pre-equilibrium between the zerovalent palladium complex and the vinylic halide prior to an irreversible oxidative addition:[10]



$$\text{CH}_2{=}\text{CH}{-}X + Pd^0(dppf)(cot) \rightleftharpoons \{\eta^2\text{-}(\text{CH}_2{=}\text{CH}X), Pd^0(dppf)(cot)\} \rightarrow \text{etc.} \qquad (3)$$

Scheme I. Rates and Mechanism of the Reversible Oxidative Addition of Z and E 1,2-Dichloroethylene to Low-Ligated Zerovalent Palladium



To the best of our knowledge, there is no established kinetic proof of the overall irreversibility of oxidative additions, and even

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* Author to whom any correspondence should be addressed.

[†] Dedicated to the memory of Prof. J. K. Stille.

(1) For reviews see e.g.: (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E.-I. *Acc. Chem. Res.* **1982**, *15*, 340. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(2) For substitution at sp^2 carbon center, see e.g. ref 1, 3, and: (a) Yamamura, M.; Moritani, I.; Murahashi, S.-I. *J. Organomet. Chem.* **1975**, *91*, C39. (b) Fauvarque, J.-F.; Jutand, A. *Bull. Soc. Chim. Fr.* **1976**, *5-6*, 765. (c) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. (d) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, *19*, 191. (e) Okukado, N.; van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (f) Negishi, E.-I.; Okukado, N.; King, A. O.; van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (g) Murahashi, S.-I.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408. (h) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron Lett.* **1981**, *22*, 127. (i) Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 959. (j) Fauvarque, J.-F.; Jutand, A. *J. Organomet. Chem.* **1981**, *209*, 109. (k) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (l) Ratovelomana, V.; Linstrumelle, G.; Normant, J.-F. *Tetrahedron Lett.* **1985**, *26*, 2575. (m) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (n) Minato, A.; Susuki, K.; Tamao, K. *J. Am. Chem. Soc.* **1987**, *109*, 1257. (o) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (p) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031 and references therein.

(3) For use of vinylic dihalides in the palladium-catalyzed synthesis of stereodefined natural product intermediates see e.g.: (a) Ratovelomana, V.; Linstrumelle, G. *Tetrahedron Lett.* **1981**, *22*, 315. (b) Ratovelomana, V.; Linstrumelle, G. *Tetrahedron Lett.* **1984**, *25*, 6001. (c) Guillerm, D.; Linstrumelle, G. *Tetrahedron Lett.* **1985**, *26*, 3811. (d) Carpita, A.; Rossi, R. *Tetrahedron Lett.* **1986**, *27*, 4351. (e) Andreini, B. P.; Benetti, M.; Carpita, A.; Rossi, R. *Tetrahedron* **1987**, *20*, 4591.

(4) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (c) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (d) Moravsky, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (e) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (f) Negishi, E.; Takahashi, T.; Baba, S.; van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (g) See e.g.: Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353.

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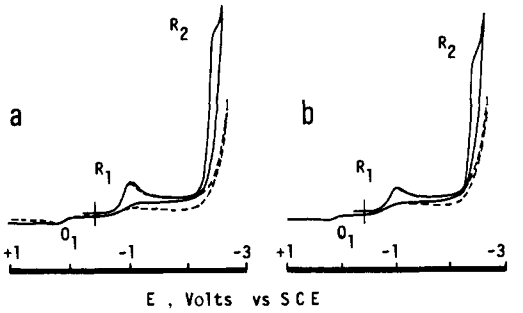

Figure 1. Cyclic voltammetry of Pd^{II}(PPh$_3$)$_2$Cl$_2$ (2 mM) in THF, 0.3 M n-Bu$_4$NBF$_4$, in the absence (dashed curves) or in the presence of 1 equiv of (a) (E)- or (b) (Z)-1,2-dichloroethylene (solid curves) at a gold disk electrode (ϕ 0.5 mm). Scan rate 0.2 V·s^{-1}, 20 °C.

indications of the opposite (vide infra). Moreover, an equivalent reverse step is invoked for *cis*-σ-vinylpalladium[11] complexes as an obligatory component of catalytic cycles leading to nucleophilic substitution (step iii in Scheme I).

We wish to report here a detailed kinetic investigation of the mechanism of oxidative addition of 1,2-dichloroethylene (Z or E)[12] to a low-ligated zerovalent palladium complex obtained by electrochemical reduction of the ubiquitous Pd^{II}(PPh$_3$)$_2$Cl$_2$.

Results and Discussion

Electrogeneration of σ-Vinylpalladium Complexes. In the absence of 1,2-dichloroethylene, the electrochemical reduction of Pd^{II}(PPh$_3$)$_2$Cl$_2$ occurs via an overall two-electron irreversible process at wave R$_1$ (E^p −1.0 V vs SCE at 0.2 V·s^{-1} in Figure 1) to afford quantitatively zerovalent palladium species.[6b,13] The number and nature of these zerovalent species depend on the exact reaction conditions.[14] Under the conditions of millimolar concentrations of palladium complex considered in this study, and in the absence of purposedly added halide ions, the reaction leads to the formation of Pd^0(PPh$_3$)$_2$Cl$^-$,[14] which will be referred to as "Pd^0" in the following. Irreversible oxidation of this species occurs at wave O$_1$ (E^p 0.1 V vs SCE at 0.2 V·s^{-1}) via an irreversible two-electron process.[6b]

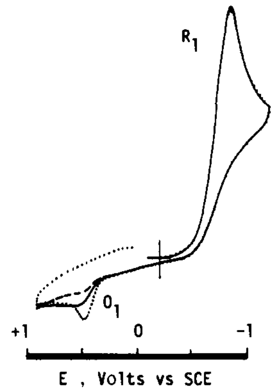

Figure 2. Cyclic voltammetry of Pd^{II}(PPh$_3$)$_2$Cl$_2$ (2 mM) in THF, 0.3 M n-Bu$_4$NBF$_4$, in the absence (dotted curve) or in the presence of 10 equiv (solid curve) or 20 equivs (dashed curve) of (E)-1,2-dichloroethylene at a gold disk electrode (ϕ 0.5 mm). Scan rate 0.2 V·s^{-1}, 0 °C.

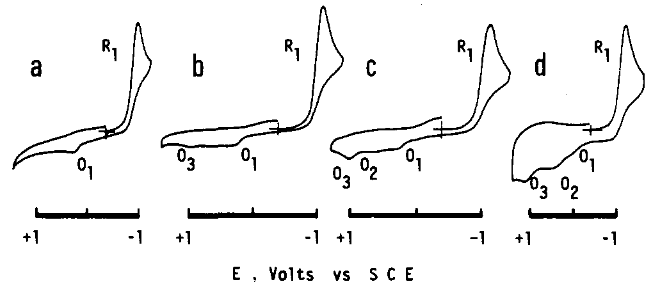

Figure 3. Cyclic voltammetry of Pd^{II}(PPh$_3$)$_2$Cl$_2$ (2 mM) in THF, 0.3 M n-Bu$_4$NBF$_4$, in the presence of 10 equiv of (E)-1,2-dichloroethylene at a gold disk electrode (ϕ 0.5 mm in a, b, c; ϕ 0.125 mm in d). Scan rates (a) 0.2, (b) 2.0, (c) 10, and (d) 100 V·s^{-1}; 0 °C.

Wave R$_1$ is not affected by the presence of one or several equivalents of (Z)- or (E)-1,2-dichloroethylene. However, when the scan is extended to more negative values a new wave, R$_2$, is observed (E^p −2.38 V vs SCE at 0.2 V·s^{-1} or E^p −2.43 V vs SCE at 0.2 V·s^{-1} respectively for the (Z)- or (E)-dichloroalkene), as illustrated by Figure 1. Comparison with authentic materials[8a] suggests that these waves feature respectively the reduction of a (Z)- or (E)-σ-vinylpalladium complex ClCH=CHPd^{II}(PPh$_3$)$_2$Cl.[15] This indicates that during the cathodic scan the zerovalent palladium generated at wave R$_1$ reacts with the 1,2-dichloroethylene to afford the corresponding oxidative addition product:

$$\text{Pd}^0 + (Z \text{ or } E)\text{-ClCH=CHCl} \rightarrow (Z \text{ or } E)\text{-ClCH=CHPd}^{II}(\text{PPh}_3)_2\text{Cl} \quad (4)$$

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(5) (a) Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186. (b) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. (c) Ugo, R. *Coord. Chem. Rev. A* **1972**, *7*, 245. (d) Rosevear, D. T.; Stone, F. G. A. *J. Chem. Soc.* **1968**, 164.

(6) (a) Negishi, E.-I.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338. (b) For electrochemical generation of similar intermediates see: Amatore, C.; Azzabi, M.; Jutand, A. *J. Organomet. Chem.* **1989**, *363*, C41.

(7) For a discussion of this point, see e.g. ref 4g and: Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434 and references therein.

(8) (a) Fitton, P.; McKeon, J. E. *Chem. Commun.* **1968**, 4. (b) Anderson, J. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185. (c) Compare to the similar situation for platinum complexes in: Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103. (d) Note however that cis complexes have been isolated in oxidative addition of sterically hindered aryl halides to zerovalent palladium: Urata, H.; Tanaka, M.; Fuchikami, T. *Chem. Lett.* **1987**, 751.

(9) Brown, J. M.; Cooley, N. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1345.

(10) For other examples of Pd^0 olefinic complexes see e.g. ref 8a and: (a) Green, M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 449. (b) Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *Organometallics* **1988**, *7*, 1761. (c) For the kinetic irreversibility of the overall oxidative addition see: Crabtree, R. H. In *The Organometallic Chemistry of Transition Metals*; Wiley: New York, 1988; pp 42 and 123. (d) However, under some circumstances reductive elimination of aryl halides has been reported [Ettore, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45]: Pt(PEt$_3$)$_2$(Ph)$_2$I$_2$ → *trans*-Pt(PEt$_3$)$_2$PhI + PhI.

(11) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Although it is considered that *trans*-σ-vinylpalladium species do not undergo reductive elimination, the two σ-vinylpalladium species in Scheme I are often written as trans complexes,[1c,11a] except when chelating ligands are used.[4g] Also a slow rate of cis/trans isomerization [see later and (a) above] is difficult to reconcile with the large efficiency typical of these catalytic cycles.[1-3] We therefore favor the intervention of *cis*-σ-vinylpalladium species (vide infra). (c) Note however that the rate of cis/trans isomerization may be greatly increased by the presence of an excess of phosphine ligand: Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.

(12) The choice of this substrate was suggested to us by G. Linstrumelle owing to its synthetic implications.[3]

(13) Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45.

(14) (a) Three palladium species are in rapid equilibrium: Pd^0(PPh$_3$)$_2$Cl$^-$, Pd^0(PPh$_3$)$_2$Cl$_2^{2-}$, and a dimeric [Pd^0(PPh$_3$)$_2$Cl]$_2^{2-}$, according to the initial concentration of the divalent palladium precursor complex as well as of that of purposedly added chloride ions. Amatore, C.; Azzabi, M.; Jutand, A. Unpublished results to be reported separately. (b) Compare ref 6.

(15) (a) Since *cis*-σ-vinylpalladium complexes are not stable enough to be prepared as authentic samples, the assignment of waves R$_2$ is made on the basis of the electrochemistry of the trans derivatives. However it is expected that the reduction waves of the cis and trans derivative occur in similar potential ranges, since it involves the cleavage of the palladium–chlorine bond. (b) In the presence of 1 equiv (or less) of dihaloalkene this process is expected to be followed by a second electron transfer and cleavage of the carbon–palladium bond which should produce a Pd^0 species. (c) In the presence of excesses of dihaloalkene waves R$_2$ show a marked catalytic character.[16] Compare to a similar situation for the cross coupling of aryl halides by electrogenerated low-ligated Ni^0: Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203.

(16) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806 and references therein. (c) Andrieux, C. P.; Savéant, J.-M. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, Chapter 7, pp 305–390.

In apparent contradiction[17] with the existence of this facile reaction, wave O_1 is still detected on the anodic trace, whether the cathodic scan is interrupted before or after wave R_2,[15b] provided that the voltammograms are performed at room temperature or at relatively slow scan rates (vide infra). At 0 °C or lower, although the general features of the cathodic portions of the voltammograms remain identical with those described above, the shape of wave O_1 is considerably affected.[18a] As shown in Figure 2, wave O_1 has the appearance of a plateau instead of a well-resolved peak shape and tends to vanish upon increasing the vinylic chloride concentration. Such a peculiar behavior, typical of an electrochemical "CE" mechanism,[18b] indicates that the zerovalent palladium species oxidized at wave O_1 is present at trace levels within the solution near the electrode but is slowly regenerated chemically at the electrode surface by continuous displacement of an endergonic equilibrium. On the other hand, we know from the relative magnitude of the R_1 and R_2 waves observed on the cathodic part of the voltammograms that the zerovalent palladium electrogenerated at wave R_1 is quantitatively converted to a σ-vinylpalladium(II) (also vide infra) complex in the solution. We are then forced to admit that this reaction is reversible within the time scale of cyclic voltammetry[18b]

$$\begin{array}{l}(Z\text{ or }E)\text{-ClCH}{=}\text{CHPd}^{\text{II}}(\text{PPh}_3)_2\text{Cl}\ \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}}\\ \qquad\qquad \text{Pd}^0 + (Z\text{ or }E)\text{-ClCH}{=}\text{CHCl} \qquad (5)\\ \qquad\qquad \Big\downarrow [-2e]\\ \qquad\qquad \text{etc.}\end{array}$$

and is continuously displaced to its right-hand side by the irreversible oxidation of Pd^0 occurring at wave O_1. At room temperature and low scan rates this process must be sufficiently rapid for wave O_1 to behave as a pure diffusion wave. At lower temperatures this process is expected to become slower both for kinetic and thermodynamic reasons,[19] which leads to the observance of a characteristic CE behavior[18b] as shown on Figure 2.

In order to ascertain the validity of the above analysis, a voltammetric investigation of the problem was performed as a function of increasing scan rates, i.e. decreasing the reaction time. Figure 3 presents an illustration of the distortions observed upon increasing the scan rate for the voltammograms of the Pd^{II}/Pd^0 system in the presence of (*E*)-1,2-dichloroethylene. Although wave O_1 is the main oxidation wave observed at the lowest scan rates (≈ 0.1 V·s^{-1}), it tends to vanish when the scan rate is increased (≈ 10–100 V·s^{-1}) and to be replaced by a new wave O_3 which grows in at more positive potentials. Notably, this change in the oxidative part of the voltammograms is not associated with a change in the cathodic trace: wave R_2, observed when the potential is extended more negatively, and wave R_1 remain unaffected.[20] When the scan rate is further increased (≈ 1000 V·s^{-1}) wave O_3 decreases and is gradually replaced by the combination of wave O_1 with a new wave O_2.[21] This decay is associated with a concomitant disappearance of wave R_2, which is seen upon extending the scan more negatively.

The simplest qualitative way to rationalize such a dynamic behavior is that the product reduced at wave R_2 and oxidized at wave O_3 results from the oxidative addition in eq 4. For reaction times comparable to the half-life of Pd^0, i.e. for scan rates in the kV·s^{-1} range, the reaction is not complete so that R_2 and O_3 waves are not totally developed and zerovalent species are still detected at waves O_1 and O_2. For longer reaction times, i.e. for intermediate scan rates, the reaction is complete, as shown by the full magnitude of the R_2 and O_3 waves. However as concerns wave O_3 this remains true only provided that the reaction time is short enough, or the temperature low enough, for the equilibrium in eq 5 to be frozen. At even smaller scan rates the reductive elimination equilibrium in eq 5 is slowly displaced to its right-hand side because of the oxidation of Pd^0 which occurs at wave O_1. This results in a decrease of wave O_3, associated with an increase of the oxidation wave O_1. For scan rates under 1 V·s^{-1} at room temperature the overall sequence in eq 5 behaves almost as a fully dynamic equilibrium, so that only the first oxidation wave, O_1, is observed (Figure 1).

***cis*-σ-Vinylpalladium Complex as an Intermediate.** The dynamic interchange and shape modifications of wave R_2 and of the triad of waves O_1, O_2, and O_3 are perfectly characteristic of a rapid and reversible oxidative addition of (*Z* or *E*)-1,2-dichloroethylene to Pd^0. Within this kinetic framework we want to discuss the nature of the intermediates observed at waves R_2 and O_3 as well as that at wave O_2.[21] Let us first discuss the nature of the product observed at waves R_2 and O_3. Since wave R_2 is identical within the accuracy of the measurements to that of an authentic *trans*-σ-vinylpalladium complex (*Z* or *E* respectively), one expects this complex to be the product of the oxidative addition considered in eqs 4 or 5. Furthermore this is consistent with chemical intuition.

A major argument against this attribution is provided by the time evolution of the ^{31}P NMR spectra of a solution obtained after electrolysis of $Pd^{II}(PPh_3)_2Cl_2$ in the presence of (*E*)-1,2-dichloroethylene at room temperature. Immediately after electrolysis the spectrum consists of a broad signal (Δ 420 Hz) at 19.77 ppm (162 MHz vs H_3PO_4 in THF, 0.1 M *n*-Bu_4NBF_4) and of a sharp peak at 23.91 ppm. The downfield peak is identical with that observed (23.73 ppm) for an authentic sample of *trans*-σ-(*E*)-vinylpalladium[8a] complex under the same conditions. With time the sharp peak grows at the expense of the broad one and is the only peak observed after 2.5 h. Therefore the species reduced at wave R_2 or oxidized at wave O_3 within a voltammetric time scale (i.e. under a second) cannot be a *trans*-σ-vinylpalladium complex, formed at much longer times, but one of its immediate precursors, viz. a *cis*-σ-vinylpalladium or possibly an (η^2-dichloroalkenyl)palladium(0) species as observed by Brown et al. in a related study.[4g,9]

In favor of a *cis*-σ-vinylpalladium is the observation of a reduction wave R_2 almost identical with that obtained for an authentic sample of the *trans*-σ-vinylpalladium. Indeed one expects

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[17] During the cathodic scan Pd^0 is electrogenerated within the diffusion layer adjacent to the electrode and reacts quantitatively with the dichloroalkene as evidenced by the magnitude of wave R_2. Therefore during the anodic scan no wave featuring Pd^0 oxidation should be observed. See e.g. EC mechanisms in refs 16a and 16c and: Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.

[18] (a) The decrease of wave O_1 (i.e. the decrease of Pd^0 concentration at the electrode surface) when temperature is *decreased* is a priori inconsistent with any kinetic situation, except those where Pd^0 is involved in a rapid equilibrium with a positive $\Delta H°$.[19] (b) In the electrochemical nomenclature "CE" mechanisms refer to the following sequence involving an up-hill equilibrium prior to electron transfer:

$$\text{I} \rightleftharpoons \text{A}\ (K \ll 1)$$

$$\text{A} \pm e \rightarrow \text{etc}$$

Compare e.g.: (c) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 445–448. (d) Savéant, J.-M.; Vianello, E. *Electrochim. Acta* **1963**, *8*, 905. (e) Nicholson and Shain in ref 16a.

[19] The reductive elimination in eq 5 is expected to have a positive enthalpy, and therefore $\delta(\ln K)/\delta T = \Delta H°/RT^2 > 0$. Indeed from the electrochemical behavior of the system, we know that $K \ll 1$, i.e. that $\Delta G° > 0$. On the other hand the entropy of the reaction is expected to be positive and in the range of +30 eu owing to its dissociative character. Thus $\Delta H° = \Delta G° + T\Delta S° > 0$.

[20] (a) Wave R_1 not being affected over the whole range of scan rates is taken as an internal standard to evaluate the relative sizes of waves R_2, O_1, O_2, and O_3 to eliminate the intrinsic effect of the scan rate on peak currents (i.e.: $i^p \propto v^{1/2}$; see e.g. ref 18c, p 218). (b) In the presence of excesses of the dihaloalkene one observes variations for wave R_2 owing to the decreased efficiency of the redox-catalysis phenomenon[15c] at high scan rates.[16]

[21] (a) Note that at the highest scan rates where O_3 has almost disappeared, the observation of a set of waves O_1 and O_2 rather than of wave O_1 only establishes[18] that the reductive elimination in eq 5 does not occur in a single step but proceeds at least through an intermediate, I, whose oxidation is observed at wave O_2:

$$cis\text{-Pd(II)} \underset{k_{-\alpha}}{\overset{k_\alpha}{\rightleftharpoons}} \text{I} \underset{k_{-\beta}}{\overset{k_\beta}{\rightleftharpoons}} \text{Pd}^0 \rightarrow \text{etc.}$$

with $(k_\alpha/k_{-\alpha}) \ll 1$, $(k_\beta/k_{-\beta}) \ll 1$. (b) Owing to the order of appearance of the waves as a function of scan rate, one also has $k_\beta k_{-\beta}^{1/2} \gg k_\alpha k_{-\alpha}^{1/2}$.[18]

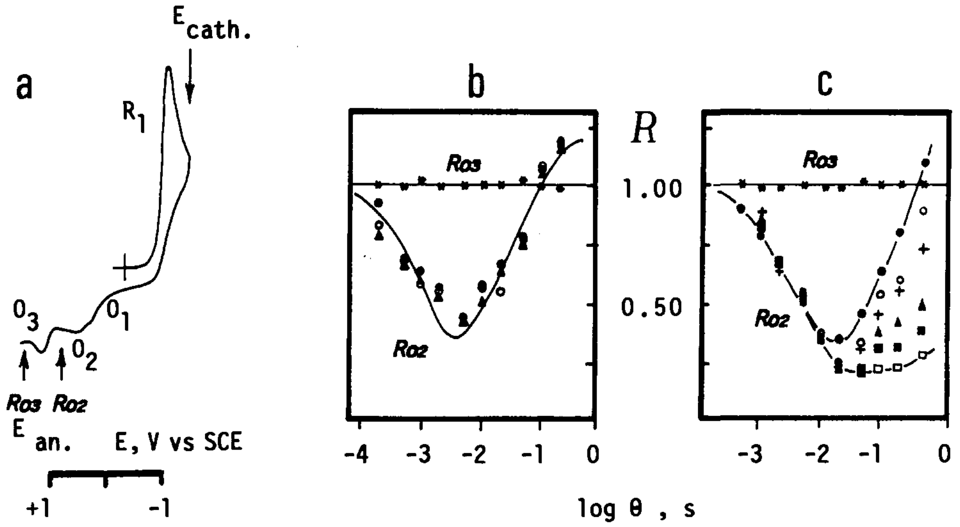

Figure 4. Double potential step chronoamperometry of $Pd^{II}(PPh_3)_2Cl_2$ (2 mM) in THF, 0.3 M *n*-Bu_4NBF_4, in the presence of (*Z*)- or (*E*)-1,2-dichloroethylene at a gold disk electrode (ϕ 0.5 mm, $\theta \geq 2$ ms; ϕ 0.125 mm, $\theta \leq 2$ ms); 0 °C. (a) Location of the cathodic ($E_{cath.}$) and of the anodic ($E_{an.}$) potential steps shown on the cyclic voltammogram of $Pd^{II}(PPh_3)_2Cl_2$ (2 mM) in the presence of 5 equiv of (*E*)-1,2-dichloroethylene under the same conditions, at 50 $V{\cdot}s^{-1}$. (b, c) Variations of the normalized current ratios R_{O2} and R_{O3} (*) as a function of the potential step duration, θ, and of the concentration of dichloroethylene. (b) (*Z*)-1,2-Dichloroethylene, 200 (●), 300 (▲), and 400 (○) equiv. Solid line: theoretical variations (compare Figure 5) of R_{O2} for $k_2 = 360\ s^{-1}$ and $k_{-2} = 45\ s^{-1}$. (c) (*E*)-1,2-Dichloroethylene, 5 (●), 10 (○), 20 (+), 50 (▲), 100 (■), and 200 (□) equiv. Solid lines are drawn to emphasize the two extreme data sets (compare Figure 6).

the reduction of *trans*- and *cis*-σ-vinylpalladium(II) complexes to occur at very similar potentials,[15a] whereas that of an η^2-coordinated alkene palladium species should be observed at more negative potentials since it involves a zerovalent palladium-centered species. The observation of the O_3 oxidation wave may appear surprising in this respect since authentic samples of neither (*Z*)- nor (*E*)-*trans*-σ-vinylpalladium[8a] complexes present any oxidation wave under the conditions investigated. However, from electrochemical studies of related species involving a dppe chelating ligand, we know that cis-constrained derivatives present an oxidation wave in the region where wave O_3 is observed.[22]

A second argument in favor of a *cis*-σ-vinylpalladium(II) as opposed to an η^2-coordinated palladium(0) species is based on the observation, for the highest scan rates ($\approx$1000 $V{\cdot}s^{-1}$), of the couple of O_2 and O_1 waves, instead of wave O_1 only. Within the dynamic framework of antecedent chemical reaction mechanisms this indicates that the species oxidized at wave O_2 is an intermediate on the route between Pd^0 (oxidized at wave O_1) and the product oxidized at wave O_3. On the other hand the close proximity of the two waves O_1 and O_2 suggests that the chemical nature of this intermediate does not strongly differ from that of Pd^0.[23] On the basis of Brown's results,[4g,9] it is reasonable to propose that the intermediate observed at wave O_2 is the η^2-coordinated palladium(0)[10,24] precursor of the cis derivative and therefore that the intermediate observed at waves R_2 or O_3 is the *cis*-σ-vinylpalladium(II) derivative.

On the basis of the above qualitative analysis of the cyclic voltammetry of $Pd^{II}(PPh_3)_2Cl_2$ in the presence of (*Z*)- or (*E*)-1,2-dichloroethylene we propose that the oxidative addition to the low-ligated electrogenerated zerovalent palladium occurs in two steps (eqs 7 and 8) to afford the corresponding *cis*-σ-vinylpalladium(II) which evolves in a much longer time scale to the *trans*-σ-vinylpalladium(II) (eq 9). A more complete kinetic

$$Pd^{II}(PPh_3)_2Cl_2 \xrightarrow{+2e} Pd^0 \qquad (6)$$

$$Pd^0 + ClCH{=}CHCl \underset{}{\overset{fast}{\rightleftharpoons}} \{\eta^2\text{-}ClCH{=}CHCl,\ Pd^0\} \qquad (7)^{24}$$

$$\{\eta^2\text{-}ClCH{=}CHCl,\ Pd^0\} \underset{slow}{\overset{fast}{\rightleftharpoons}} cis\text{-}ClCH{=}CHPd^{II}(PPh_3)_2Cl \qquad (8)$$

$$cis\text{-}ClCH{=}CHPd^{II}(PPh_3)_2Cl \xrightarrow{slow} trans\text{-}ClCH{=}CHPd^{II}(PPh_3)_2Cl \qquad (9)^{11b}$$

characterization of the reaction sequence in eqs 7 and 8 by cyclic voltammetry is hampered by the fact that each of the waves observed by the system is controlled by electron-transfer kinetics.[25] A detailed treatment of eqs 7 and 8 on the basis of cyclic voltammetry would then require the independent knowledge of additional kinetic and thermodynamic parameters ($E°$, k_0, and α for each intermediate). We therefore decided to rely on a double potential step chronoamperometric analysis[26] which is independent of such parameters.[27]

Kinetics of Oxidative Addition of (*Z*)-1,2-Dichloroethylene to Pd^0. When the first potential step is made on the plateau of wave R_1 (see Figure 4a), $Pd^{II}(PPh_3)_2Cl_2$ is converted to the low-ligated zerovalent palladium complex, Pd^0,[14] which undergoes follow-up chemical reaction in the diffusion layer adjacent to the electrode. After a time period θ the current $i_c(\theta)$ is measured and a second potential step of duration θ is performed on the plateau of wave O_3. The anodic current $i_{a,O3}(\theta)$, measured at the end of this second step, is then directly related to the concentration of all the species present in the diffusion layer oxidizable at the applied potential. From the above analysis in cyclic voltammetry, this includes the

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[22] (a) For example, authentic samples of *trans*-Ph-$Pd^{II}I(PPh_3)_2$ or of *cis*-Ph-$Pd^{II}I$(dppe) are reduced respectively at −2.0 and −1.8 V vs SCE (E^p at 0.2 $V{\cdot}s^{-1}$) in THF (0.2 M). *trans*-Ph-$Pd^{II}I(PPh_3)_2$ is not oxidizable before the solvent discharge, whereas *cis*-Ph-$Pd^{II}I$(dppe) is oxidized at +1.1 V vs SCE (E^p at 0.2 $V{\cdot}s^{-1}$). Amatore, C.; Azzabi, M.; Jutand, A. Unpublished results to be reported separately. (b) This difference between cis and trans isomers may be tentatively related to the existence of a facile reductive elimination upon oxidation for the cis species whereas this reaction is impossible for a trans derivative without involving an isomerization. Compare e.g.: (c) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262. (d) Almemark, M.; Akermark, B. *J. Chem. Soc., Chem. Commun.* **1978**, 66.

[23] This close structural identity between Pd^0 and the intermediate, I, oxidized at wave O_2 (by comparison to that oxidized at wave O_3) is also supported by the fact that the equilibrium between Pd^0 and I is considerably more labile than that between I and the product oxidized at O_3.[21b]

[24] In the following we will refer to the intermediate oxidized at wave O_2 as an η^2-dihaloalkene palladium(0).[4g,9,10] However, the dihalo alkene may also be coordinated through palladium–chlorine interactions.

[25] Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1971**, *48*, 113.

[26] (a) Reference 18c, pp 136–146. For application to systems including CE components see e.g.: (b) Hanafey, M. K.; Scott, R. L.; Reilley, C. N. *Anal. Chem.* **1978**, *50*, 116. (c) Amatore, C.; Garreau, D.; Hammi, M.; Pinson, J.; Savéant, J.-M. *J. Electroanal. Chem.* **1985**, *184*, 1. (d) Lee, K. Y.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.*, in press.

[27] In chronoamperometric methods, when the potential steps are performed on the diffusion plateau of the waves, the current is independent of the kinetics of electron transfer.[26a]

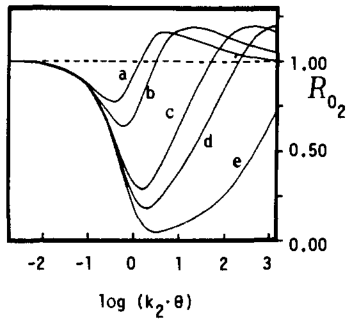


Figure 5. Theoretical variations of R_{O2} as a function of the potential step duration, θ, and of the rate constants k_2 and k_{-2}. (k_{-2}/k_2): 1 (a), 0.5 (b), 0.1 (c), 0.05 (d), and 0.01 (e).

species oxidized at waves O_1, O_2, and O_3 (compare Figure 4a). If all the zerovalent palladium electrogenerated during the first step is chemically "stored" in the form of these species, i.e. without the involvement of other chemical routes, one expects the ratio $|i_{a,O3}(\theta)/i_c(\theta)|$ to be equal to $(1 - 2^{-1/2}) \approx 0.293$.[28] Thus the normalized current ratio

$$R_{O3} = |i_{a,O3}(\theta)/i_c(\theta)|/(1 - 2^{-1/2}) \qquad (10)$$

should be equal to unity. The results obtained at different times θ ranging from 0.2 ms to 0.2 s, represented on Figure 4b, show that $R_{O3} = 1$ within the limits of experimental accuracy. One can thus consider that the sum of the concentration of the species detected at waves O_1, O_2, and O_3 represents quantitatively the concentration of Pd^0 electrogenerated at wave R_1.[28]

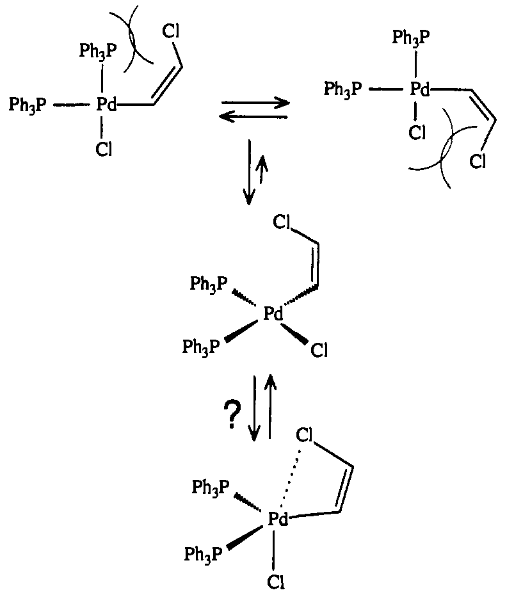
Similarly $R_{O2} = |i_{a,O2}(\theta)/i_c(\theta)|/(1 - 2^{-1/2})$ is determined when the second step is made on the plateau of wave O_2. Then R_{O2} represents the fraction of palladium existing[29] under the form of the products oxidized at waves O_1 and O_2. Figure 4b presents the variations of R_{O2} as a function of the step duration and of the concentration of (Z)-1,2-dichloroethylene. A first observation is that R_{O2} does not depend on the dihaloalkene concentration. This demonstrates[30] that the equilibrium between Pd^0 and the η^2 complex in eq 11 is totally displaced to its right-hand side ($k_1/k_{-1} \gg 1$ M^{-1}) under the conditions used in Figure 4b, a necessary requirement for the observation of kinetics with zero order in dichloroalkene. Inspection of Figure 4b shows that at short times ($\theta < 5$ ms) the concentration of the η^2 complex decays with time, whereas it increases with time at longer times ($\theta > 5$ ms). This behavior is in complete agreement with the qualitative deductions based on cyclic voltammetry. It occurs because at short times the backward reaction of the oxidative addition step (eq 12) is outrun. Then one observes a first-order disappearance of the η^2

$$Pd^0 + ClCH{=}CHCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{\eta^2\text{-}ClCH{=}CHCl, Pd^0\} \qquad (11)$$

$$\{\eta^2\text{-}ClCH{=}CHCl, Pd^0\} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis\text{-}ClCH{=}CHPd^{II}(PPh_3)_2Cl \qquad (12)$$

complex with almost no interference of the backward reaction. On the other hand at longer reaction times, the backward reaction plays a significant role, and all the palladium(0) which had reacted at shorter times can be regenerated at the electrode surface owing to the continuous displacement of eq 12 to its left-hand side resulting from the oxidation of Pd^0 and of the η^2 complex by the electrode. In other words the descending branch of the curve in Figure 4b, observed at shorter times, is mainly controlled by the magnitude of k_2 (eq 12) whereas the rising branch at longer times depends both on k_2 and k_{-2}.[29b] By comparison to the working curve[26b] shown as the solid line in Figure 4b (compare Figure 5), this allows the determination of $k_2 = 360$ s^{-1} and $k_{-2} = 45$ s^{-1}.

Scheme II. Rates and Mechanism of the Reversible Oxidative Addition of Z and E 1,2-Dichloroethylene to Low-Ligated Zerovalent Palladium



Kinetics of Oxidative Addition of (*E*)-1,2-Dichloroethylene to Pd^0. Figure 4c shows that essentially identical behavior is observed for the E isomer. R_{O3} is equal to unity independent of the step duration time θ, and R_{O2} decays for short step times and increases at longer times. However it is seen that while the descending branch remains independent of the vinylic chloride concentration as in the case of the Z isomer, the rising branch depends strongly on this parameter. By comparison to the set of working curves in Figure 5 this shows that k_2 and eq 12 remains constant when the (E)-dichloroethylene concentration is increased whereas k_{-2} decreases. Fitting of the experimental data of Figure 4c to the working curves in Figure 5 confirms this interpretation as evidenced by Figure 6 and allows one to determine $k_2 = (100 \pm 10)$ s^{-1} and to quantify the apparent variations of k_{-2} with the alkene concentration, noted [alk] (in M):

$$(k_{-2})^{ap}\ (s^{-1}) = (8.7 \pm 0.9)/(1 + 10.5[alk]) \qquad (13)$$

In order to remain consistent with the principle of microscopic reversibility one is then forced to consider that for the case of the E isomer, the oxidative addition in eq 12 consists of a sequence of two reactions: the oxidative addition (eq 15) itself, followed

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[28] (a) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1980**, *107*, 353. (b) Under the present circumstances this establishes also that each oxidation wave O_1, O_2, and O_3 involves two electrons per palladium center.

[29] (a) For CE mechanisms this includes also the fraction of palladium amenable to oxidation because of the displacement of the equilibria in eqs 7 and 8. (b) This explains the observation of R_{O2} values larger than unity at large θ values (compare Figures 4b,c, 5 and 6). Indeed the fraction of zerovalent palladium which has undergone an almost irreversible reaction at short times, i.e. when the backward reaction in eq 8 was outrun, tends to be entirely restored at longer times.[26b,c]

[30] In a general case (provided one assumes the existence of a kinetic steady state applying to the (η^2-ClCH=CHCl, Pd^0) labile complex) the homogeneous kinetic term to be considered in the partial derivative equation[31] controlling the time dependence of [S], the sum of the concentrations of the two species oxidized at waves O_1 and O_2, is given by

$$d[S]/dt = -d[cis]/dt = -\{k_1k_2[alk][S] - k_{-2}(k_1[alk] + k_{-1})[cis]\}/\{k_1[alk] + k_{-1} + k_2\}$$

where the rate constants k_j are defined in eqs 11 and 12; [cis] represents the concentration of the intermediate oxidized at wave O_3 and [alk] that of the dichloroalkene. Such an expression predicts a complex dependence of [S] and therefore of R_{O2} on the concentration of the dichloroalkene. However, in the limiting situation where $k_1[alk] \gg (k_{-1} + k_2)$, i.e. when the equilibrium in eq 11 is more labile than that in eq 12 and is totally shifted to its right-hand side, the above expression simplifies to

$$d[S]/dt = -d[cis]/dt = -k_2[S] + k_{-2}[cis]$$

which demonstrates that [S], and therefore R_{O2}, does not depend on the alkene concentration.

[31] (a) Reference 18c, pp 435–436. (b) Amatore, C. In *Organic Electrochemistry*, 3rd ed.; Lund, H., Baizer, M., Eds.; Dekker: New York, in press; Chapter 2.

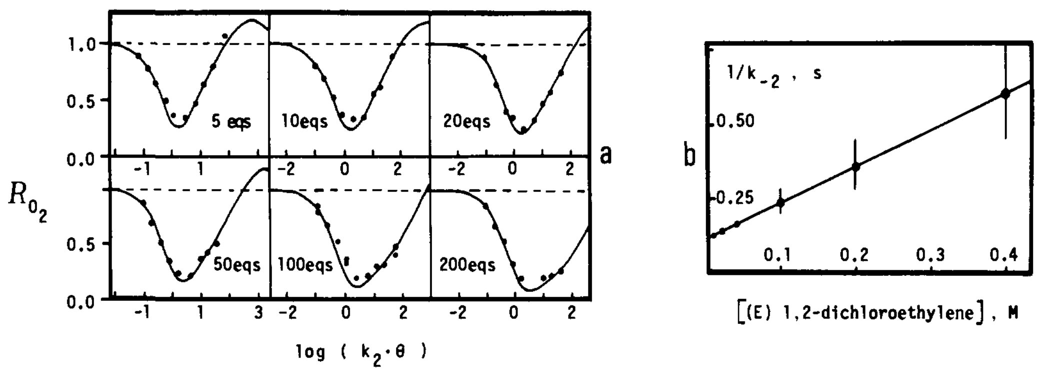


Figure 6. (a) Comparison between the data in Figure 4c and the working curves in Figure 5, as a function of the (*E*)-1,2-dichloroethylene concentration, for the following rate constants: $(k_2)^{ap}$ = 125 (5 equiv), 100 (10, 20, 50, and 100 equiv), and 90 s^{-1} (200 equiv); $(k_{-2})^{ap}$ = 8.0 (5 equiv), 7.2 (10 equiv), 6.0 (20 equiv), 4.2 (50 equiv), 2.8 (100 equiv), and 1.6 s^{-1} (200 equiv). (b) Variations of k_{-2} with the concentration of (*E*)-1,2-dichloroethylene.

by a rapid equilibrium involving a second alkene molecule (eq 16).[32]

$$\mathrm{Pd^0 + ClCH{=}CHCl} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \{\eta^2\text{-}\mathrm{ClCH{=}CHCl,\ Pd^0}\} \quad (14)$$

$$\{\eta^2\text{-}\mathrm{ClCH{=}CHCl,\ Pd^0}\} \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} \mathit{cis}\text{-}\mathrm{ClCH{=}CHPd^{II}(PPh_3)_2Cl} \quad (\mathit{cis}\text{-}\mathit{Pd}^{II}) \quad (15)$$

$$\mathit{cis}\text{-}\mathit{Pd}^{II} + \mathrm{ClCH{=}CHCl} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{\mathrm{ClCH{=}CHCl},\ \mathit{cis}\text{-}\mathit{Pd}^{II}\} \quad (16)$$

For such a kinetic sequence it can be shown[33] that the overall apparent rate constants, $(k_2)^{ap}$ and $(k_{-2})^{ap}$, determined in Figure 6 are given by

$$(k_2)^{ap} = k_2' = (100 \pm 10)\ \mathrm{s^{-1}} \quad (17)$$

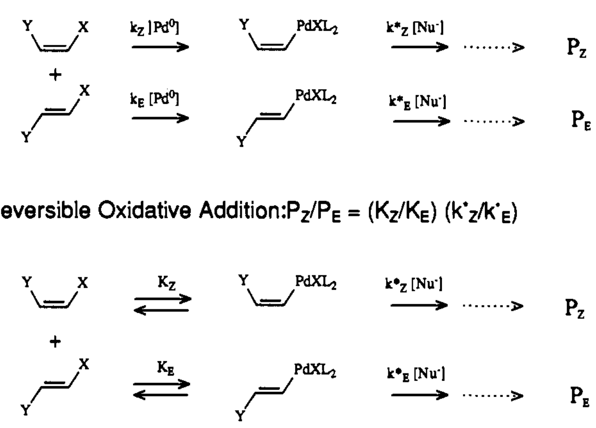
and

$$(k_{-2})^{ap} = k_{-2}'/\{1 + (k_3/k_{-3})[\mathrm{alk}]\} \quad (18)$$

Comparison to the above experimental results (eq 13) then affords $k_2' = (100 \pm 10)\ \mathrm{s^{-1}}$ and $k_{-2}' = (8{,}7 \pm 0{,}9)\ \mathrm{s^{-1}}$ for the real oxidative addition step in eq 15, and $K_3 = (k_3/k_{-3}) = 10.5\ \mathrm{M^{-1}}$ for the rapid follow-up equilibrium in eq 16.

Scheme III. Rates and Mechanism of the Reversible Oxidative Addition of Z and E 1,2-Dichloroethylene to Low-Ligated Zerovalent Palladium

A. Irreversible Oxidative Addition: $P_Z/P_E = (k_Z/k_E)$



B. Reversible Oxidative Addition: $P_Z/P_E = (K_Z/K_E)\ (k^*_Z/k^*_E)$

From the above analysis it is seen that the *Z* or *E* isomers react similarly with the electrogenerated palladium(0) species, except for the additional occurrence of a follow-up coordination of the *cis*-σ-vinylpalladium(II) complex in the case of the (*E*)-dichloroethylene. The existence of such coordination of alkyl or aryl palladium(II) complexes by olefins has already been observed.[32] Therefore one may wonder why such a step does not occur with the *Z* isomer. This discrepancy may originate from the possible involvement of the unbound chlorine atom which is pointing inward, i.e. toward the palladium center, for the *Z* isomer, whereas it points outward for the *E* isomer (Scheme II). There are two possibilities. First in the *Z* isomer this chlorine atom may sterically hinder the coordination of a second vinylic chloride. Alternatively it may coordinate to the palladium(II) center to occupy the fifth coordination site.[32]

In favor of the second hypothesis is the fact that the rate constant of the oxidation step (k_2 in eq 12 for (*Z*)-1,2-dichloroethylene, or k_2' in eq 15 for the *E* isomer) is found to be ca. four times larger for the *Z* isomer. This result, opposite to what has been observed previously[34] where the *E* isomer was found to react faster, suggests that the unbound chlorine atom provides an extra stabilization of the *cis*-σ-vinylpalladium[35] in the case of the (*Z*)-1,2-dichloroethylene.

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(32) (a) For previous examples of five-coordinate olefin complexes of palladium(II) see e.g.: Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269 and references therein. (b) However, it is not obvious if the dichloroalkene coordination in eq 16 involves the olefin as in (a) or rather a chlorine atom (compare footnote 37a).

(33) For the reaction sequence in eqs 14–16, and within the same conditions considered in footnote 30, the homogeneous term controlling the time dependence of [S] is given by

$$\mathrm{d[S]/d}t = -\mathrm{d}[\sigma]/\mathrm{d}t = -\{k_2'(k_{-3} + k_3[\mathrm{alk}])[\mathrm{S}] - k_{-2}'k_{-3}[\sigma]\}/\{k_{-2}' + k_{-3} + k_3[\mathrm{alk}]\}$$

where the rate constants are defined in eqs 15 and 16; [alk] represents the dichloroalkene concentration and [σ] the sum of the concentrations of the coordinated and uncoordinated σ-vinylpalladium species considered in both members of eq 16. Within the formalism considered in footnote 30, the above equation rewrites

$$\mathrm{d[S]/d}t = -\mathrm{d}[\sigma]/\mathrm{d}t = -(k_2)^{ap}[\mathrm{S}] + (k_{-2})^{ap}[\sigma]$$

with

$$(k_2)^{ap} = \{k_2'(k_{-3} + k_3[\mathrm{alk}])\}/\{k_{-2}' + k_{-3} + k_3[\mathrm{alk}]\}$$

and

$$(k_{-2})^{ap} = k_{-2}'\{k_{-3}/(k_{-2}' + k_{-3} + k_3[\mathrm{alk}])\}$$

When $k_{-2}' \ll (k_{-3} + k_3[\mathrm{alk}])$, i.e. when the equilibrium in eq 16 is considerably more labile than the backward reaction in eq 15, these apparent rate constants simplify to those given in eqs 17 and 18, showing that the apparent forward rate constant, $(k_2)^{ap}$, is independent of the dichloroalkene concentration, whereas the apparent backward rate constant $(k_{-2})^{ap}$ depends on this parameter.

(34) For example (*E*)-β-bromostyrene was found[2j] to react with $\mathrm{Pd^0(PPh_3)_4}$ with an overall rate constant $k^E = 10\ \mathrm{M^{-1}{\cdot}s^{-1}}$, whereas the *Z* isomer reacted with $k^Z = 1.8\ \mathrm{M^{-1}{\cdot}s^{-1}}$, i.e. $k^Z/k^E = 0.18$, to be compared to $k^Z/k^E = 3.6$ for the case of dichloroethylene.

(35) Owing to $k_2/k_{-2} \approx 8$, $\Delta G° \approx -1.20\ \mathrm{kcal{\cdot}mol^{-1}}$ for eq 12. Similarly, since $k_2'/k_{-2}' \approx 11.5$, $\Delta G° \approx -1.45\ \mathrm{kcal{\cdot}mol^{-1}}$ for eq 15. Both transition states can then be considered as rather symmetrical and partly stabilized by any possible interaction in the σ-vinylpalladium complex.

(36) The term "nucleophile" is used here in a general sense. Therefore it encompasses true nucleophiles as well as organometallic reagents.[1-3]

Consequences of the Reversibility of Oxidative Addition on the Selectivity of Palladium-Catalyzed Nucleophilic Substitution of Vinylic Halides. For the cases presented in this study, the reactions leading to the *cis*-σ-vinylpalladium intermediate can be reversed electrochemically by the irreversible consumption of $\mathrm{Pd^0}$ occurring at the electrode surface under anodic polarization. Under more classical conditions the exergonicity of the whole sequence is such that the process will behave as an irreversible one, provided that the cis derivative undergoes a follow-up reaction faster than the backward reaction leading to the η^2-coordinated $\mathrm{Pd^0}$ (eqs 12 or 15–16).[24] This justifies a posteriori the fact that oxidative addition is considered as an irreversible process under the conditions generally used for nucleophilic substitution (Scheme I).

Under such conditions, starting from a mixture of Z and E dihaloalkenes the selectivity is controlled by the rate of oxidative addition, i.e. by $K_1 = k_1/k_{-1}$ (eq 11) and k_2 (eq 12) as compared to $K_1' = k_1'/k_{-1}'$ (eq 14) and k_2' (eq 15), as shown in Scheme III-A. For the case under study, the Z isomer will react ca. 3.5 times faster than the E isomer. However, upon decreasing the nucleophile strength, the oxidative addition may become equilibrated and the selectivity be mainly controlled by the rate of nucleophile[36] entrance in the palladium coordination shell (Scheme III-B). Under these circumstances a (E)-*cis*-σ-vinylpalladium is expected to be more reactive than its Z isomer. Indeed the E isomer may undergo an easy coordination[37a] of the fifth palladium coordination site as shown by the facile reaction in eq 16, whereas such a step will be more difficult for the Z isomer because of the protection of the coordination site by the second halide atom. Thus under conditions where a mixture of Z and E vinylic dihalides is reacted, one predicts that the selectivity may be a function of the nucleophile nature. Such inversions of selectivity upon nucleophile variations have been reported. For example palladium-catalyzed cross coupling of a mixture of (E)- and (Z)-1,2-dibromoethylene[3d,38] with acetylenic nucleophiles selectively converts the E isomer into the corresponding E bromo enyne when a zinc acetylide is used. In contrast the Z derivative is selectively substituted when the nucleophile consists of an acetylenic nucleophile in the presence of copper.[37b] A similar example is given by the palladium-catalyzed cross-coupling reaction of 1,1,2-trichloroethylene. Oxidative addition to $\mathrm{Pd(PPh_3)_4}$ occurs at 80% in the 2 position and at 20% in the 1-(Z) position with only traces if any of the vinylpalladium in the 1-(E) position (see Experimental Section). Yet, reaction with an alkyl Grignard affords selectively the 1,1-dichloro-2-alkylethylene,[39a] whereas the major product is the (E)-1,2-dichloro 1-enyne derivative when an acetylenic nucleophile in the presence of copper is used.[37b,39b]

Summary and Conclusions

The experiments described here establish that the oxidative addition of 1,2-dichloroethylenes occurs via a complicated reaction sequence. First the zerovalent low-ligated palladium center coordinates to the dichloroalkene in a rapid exergonic equilibrium. The ensuing η^2 complex[24] then undergoes a reversible oxidative addition to afford a *cis*-σ-vinylpalladium intermediate which is rapidly coordinated by a second alkene molecule in the case of the (E)-1,2-dichloroethylene.[32] This last reversible step does not take place for the Z isomer within the time scale of our experiments ($\theta < 1$ s). On a much longer time scale (i.e. hours) the *cis*-σ-vinylpalladium(II) intermediate undergoes a rearrangement to the more stable trans isomer, which is the final product of the reaction. For the oxidative addition step, the Z isomer is more reactive (ca. 3.5 times) than the E isomer. By comparison to other experimental situations where E isomers are found more reactive, we believe that this behavior originates from the possibility of an intramolecular stabilization of the *cis*-vinylpalladium intermediate by coordination of the second chlorine atom to the palladium center.[37a] This effect is certainly not limited to 1,2-dihaloethylenes, but possibly may be observed whenever the 2-substituent can participate in a similar stabilizing internal coordination. For example, (Z)-1-chloro 3-enynes[3b,c,37b] are found more reactive than their E isomers.

Experimental Section

Chemicals. THF (Janssen) was stored on potassium hydroxide for 24 h and distilled from a sodium benzophenone solution under an argon atmosphere just before use. It was transferred to the cells according to standard Schlenk procedures. $n\text{-}\mathrm{Bu_4NBF_4}$ was obtained from the hydrogenosulfate salt (Janssen) by treatment with $\mathrm{NaBF_4}$ (Janssen) in water. It was further recrystallized from ethyl acetate/petroleum ether, dried under vacuum, and stored under argon before use.

(Z)- and (E)-1,2-dichloroethylene or trichloroethylene were purchased from Janssen and distilled before use. Bis(triphenylphosphine)palladium dichloride was synthesized from $\mathrm{Na_2PdCl_4}$ and $\mathrm{PPh_3}$ according to a published procedure.[5d] *trans*-$[\mathrm{ClCH{=}CHPd^{II}(PPh_3)_2Cl}]$ (E and Z) were synthesized from (Z)- or (E)-1,2-dichloroethylene and $\mathrm{Pd^0(PPh_3)_4}$ according to a published procedure.[8a] Their ^{1}H NMR spectra (250 MHz in $\mathrm{CDCl_3}$) were consistent with published ones.[8a]

^{31}P NMR spectra were performed in THF on a Bruker 162-MHz instrument with $\mathrm{H_3PO_4}$ as the internal reference.

Electrochemical Setup. Cyclic voltammetry and double potential step chronoamperometry were performed in a ca. 15-mL double-jacketed, three-electrode air-tight cell connected to a Schlenk line. The working electrode consisted of a gold disk of 0.5- or 0.125-mm diameter made from a cross-section of gold wire (Goodfellow) sealed in Pyrex glass. The reference electrode was a SCE (Tacussel) separated from the solution by a bridge (3 mL) filled with a $n\text{-}\mathrm{Bu_4NBF_4}$ solution in THF identical with that used in the cell. The counterelectrode was a platinum spiral of ca. 1 cm^2 apparent surface area located within 5 mm of the working electrode and facing it. A home-built potentiostat equipped with positive feedback for ohmic-drop compensation[40] was used. The potential waveform signal generator was an EG&G PAR Model 175 or a Tacussel GSTP4. The voltammograms and chronoamperograms were recorded with a Nicolet 3091 digital oscilloscope, and the measurements were performed on the stored curves. A MGW-Lauda M3 thermostat was used to ensure a proper temperature control.

For preparative electrochemistry a Potentiostat Tacussel PJT 35-2, if necessary boosted by a power supply in series, was used. The charge consumed was determined by integrating the electrolysis current as a function of time, with a Tacussel IG5LN. The three-electrode air-tight cell, connected to a Schlenk line, consisted of two (40 mL) compartments separated by a fritted glass No. 5. Each compartment was stirred with a magnetic Teflon-coated stir bar. The working electrode consisted of a gold grid of ca. 7 cm^2 apparent surface area, placed parallel to the fritted glass at ca. 2 cm from it. The counterelectrode was a lithium rod. The reference electrode/bridge was identical with that described above and was placed in the catholyte near the working electrode.

General Electrochemical Procedure for Cyclic Voltammetry or Double Potential Step Chronoamperometry. The cell was connected to a Schlenk line and three vacuum-argon cycles were performed. Then 12 mL of THF and 0.3 M $n\text{-}\mathrm{Bu_4NBF_4}$ (1.2 g) were introduced into the cell (3 mL of the same solution was introduced in the bridge compartment of the reference electrode) according to Schlenk techniques. After the cell was thermostated at the selected temperature, cyclic voltammograms and/or chronoamperograms were recorded over the scan rate or time range to be used in the following in order to record the background currents. $\mathrm{Pd^{II}Cl_2(PPh_3)_2}$ (4.2 to 16.8 mg, 0.5–2 mM) was then introduced in the cell and a new set of voltammograms or chronoamperograms was recorded. (E)- or (Z)-1,2-dichloroethylene (2–100 mM) was then introduced into the cell through a septum cap with a Hamilton syringe. Voltammograms and chronoamperograms were then recorded.

Owing to the difficulty of selecting the anodic step potential in chronoamperometric experiments, a series of double step chronoamperograms

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[37] (a) We ascribe the origin of this effect to the second chlorine atom, or to any (Z) substituant in the 2-position able to coordinate the palladium center,[37b] since whenever this is a group inert vis à vis palladium (e.g. an alkyl or an aryl group) the reverse trend (i.e. reaction times larger for the Z isomer than for the E isomer) is observed.[2j,34] (b) Linstrumelle, G.; Chemin, D, et al. Unpublished results to be reported. Private communication 1990.

[38] In ref 3d, a commercially available mixture E:Z (33/67) of 1,2-dibromoethylene was used.

[39] (a) Reference 21. Yields range between 55 and 81%, with a selectivity larger than 95%. (b) Yields range between 60 and 75%, with a product distribution 78:20:2 of (E)-1,2-dichloro-1-enyne:(Z)-1,2-dichloro-1-enyne:1,1-dichloro-2-enyne. The observed yields demonstrate clearly that the product distribution is not controlled by the oxidative addition only, since the σ-vinylpalladium complex precursor of the major final product (overall yield 45–60%) amounts only to 20% of the three σ-vinylpalladium complexes. (c) Note that the same reaction using a reduced form of $\mathrm{Pd^{II}Cl_2(dppb)}$ as the catalyst and aryl Grignard reagents affords the (Z)-1,2-dichloro-1-aryl derivative as the major product (55–90% yield).[2n]

[40] Amatore, C.; Lefrou, C.; Pflüger, F. *J. Electroanal. Chem.* **1989**, *270*, 43.

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were recorded for the same pulse duration θ(s), by varying the anodic step potential by 10-mV increments starting from the potential corresponding to E^p + 100 mV where E^p was the peak potential of wave O_2 (correspondingly O_3) at a scan rate v(V·s^{-1}) = 1/(40θ).[31b] The values of R_{O2} (correspondingly R_{O3}) shown in Figures 4 and 6 were selected so that, after correction from the background current, they were independent of the step potential.[41]

General Procedure for Preparative Scale Electrochemistry. THF (40 mL) and n-Bu_4NBF_4 (2.7 g) were introduced in each compartment of the cell under argon atmosphere. To be consistent with the results of transient electrochemistry, electrolyses were done on solutions 2 mM in $Pd^{II}Cl_2(PPh_3)_2$. Thus 0.08 mmol (56 mg) of $Pd^{II}Cl_2(PPh_3)_2$ and 1,2-dichloroethylene (10 equiv) were introduced in the cathodic compartment. Electrolysis was then performed at −1.4 V vs SCE and was interrupted after the current dropped to ca. 5% of its initial value. Charge integration showed that this corresponded to ca. 2 faradays per mol of $Pd^{II}Cl_2(PPh_3)_2$. For ^{31}P NMR studies, an NMR tube filled with argon and equipped with a septum was filled with this solution using a cannula according to standard Schlenk procedures.

Product Identification. For the (Z)- or the (E)-1,2-dichloroethylene, the reaction products observed within the time scale of transient electrochemistry were too unstable to be isolated and characterized (except by their ^{31}P NMR). In each case they rearranged to their thermodynamically more stable trans isomer[4b,8] which was isolated as the final product of the reaction. For example, after electrolysis, in the case of the (E)-1,2-dichloroethylene, the ^{31}P NMR spectrum consisted of a broad signal (Δ 420 Hz) at 19.77 ppm and of a sharp peak at 23.91 ppm. The peak at 19.77 ppm totally disappeared within 2.5 h while the peak at 23.91 increased concomitantly. This latter was identical with that obtained (23.73 ppm) for an authentic sample of the corresponding *trans*-σ-(E)-vinylpalladium complex.[8a]

Reaction of Trichloroethylene with $Pd^0(PPh_3)_4$. Trichloroethylene and $Pd^0(PPh_3)_4$ were reacted according to a published procedure.[8a] However, in contradiction with ref 8a, which reports only one product, i.e. *trans*-[$Cl_2C{=}CHPd^{II}(PPh_3)_2Cl$], after workup ^1H NMR (250 MHz in $CDCl_3$ relative to TMS) showed the presence of two major constituents: *trans*-[$Cl_2C{=}CHPd^{II}(PPh_3)_2Cl$] (80%; 5.10 ppm, t, J_{HP} = 0.75 Hz) and (Z)-*trans*-[$ClCH{=}CClPd^{II}(PPh_3)_2Cl$] (20%; 5.95 ppm, t, J_{HP} = 6 Hz), with a poorly resolved signal at 5.28 ppm tentatively attributable to traces of the third isomer, i.e. (E)-*trans*-[$ClCH{=}CClPd^{II}(PPh_3)_2Cl$].

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Characterization of Transition States by Isotopic Mapping and Structure–Reactivity Coefficients: Solvent and Secondary Deuterium Isotope Effects for the Base-Catalyzed Breakdown of Acetaldehyde Hemiacetals

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Abstract: Rate constants and structure–reactivity coefficients for the breakdown of acetaldehyde and acetaldehyde-d_4 hemiacetals were determined in water and deuterium oxide by trapping the acetaldehyde formed with α-effect nucleophiles. General-base catalysis by substituted acetate and cacodylate ion catalysts represents equilibrium ionization of the hemiacetal $CL_3CL(OL)OR$ (L = H or D) to form the hemiacetal anion, $CL_3CL(O^-)OR$ followed by rate-determining general-acid catalysis of the cleavage of the hemiacetal anion to form acetaldehyde and ROL. Solvent isotope effects for the catalytically active proton $k_p{}^{BH}/k_p{}^{BD}$ = 0.9–2.5 do not change significantly with changes in the pK of the catalyst or the leaving group alcohol. The increase in the secondary α,β-deuterium isotope effects $k^{\alpha\beta H}/k^{\alpha\beta D}$ = 1.21–1.30 with decreases in the pK of the leaving group alcohol can be described by the interaction coefficient $p_{yy'} = \partial\rho_n/-\partial pK_{lg} = -0.069$. The increase in Brønsted β = 0.48–0.72 with decreases in the pK of the leaving group alcohol in water can be described by the interaction coefficient $p_{xy'} = \partial\beta/-\partial pK_{lg} = 0.090$ and in D_2O by $p_{xy'} = 0.078$. The interaction coefficients and the observation of *both* solvent and secondary deuterium isotope effects are consistent with a coupling between proton transfer to the leaving group oxygen and changes in hybridization about the central carbon in the transition state for cleavage of the hemiacetal anion. The results are discussed in the context of proposals for stable hydrogen-bonded protons in concerted acid- and base-catalyzed reactions in water.

Introduction

Reaction progress or bond order in the transition state is usually estimated from kinetic isotope effects or observed structure–reactivity coefficients.[1,2] For example, an empirical approach is based on changes in Brønsted coefficients with changes in structure that can be described by interaction coefficients. The relative contributions of bond-making and bond-breaking processes in the transition state can be calculated from these interaction coefficients.[3] This approach has been used to characterize the mechanisms of the addition of nucleophiles to electrophilic carbonyl compounds as illustrated in eq 1 for the formation of hemiacetal anions.

An alternative strategy is to substitute heavy isotopes for the atoms undergoing changes in bonding. In that case, the magnitude of the kinetic isotope effect reflects the differences in vibrational

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