Rate and Mechanism of the Oxidative Addition of Vinyl Triflates and Halides to Palladium(0) Complexes in DMF

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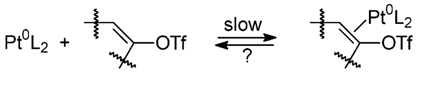
In a coordinating solvent such as DMF, the fast oxidative addition of vinyl triflates to $Pd^0(PPh_3)_4$ performed under stoichiometric conditions gives the cationic complexes $[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+TfO^-$, which have been characterized by conductivity measurements, electrospray mass spectrometry, and NMR spectroscopy, before their decomposition to vinylphosphonium salts $[\text{vinyl-}PPh_3]^+TfO^-$ and Pd^0 complexes. $[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+TfO^-$ complexes are less stable than $[(aryl)Pd(PPh_3)_2(DMF)]^+TfO^-$ formed in the oxidative addition of aryl triflates to $Pd^0(PPh_3)_4$. The rate constant of the oxidative addition of vinyl triflates and bromides to $Pd^0(PPh_3)_4$ has been determined and compared to that of aryl triflates and halides. The following reactivity orders are established in DMF: vinyl-OTf $\gg$ vinyl-Br $>$ PhBr and vinyl-OTf $\gg$ PhOTf.

Introduction

In a previous work, we established that stable cationic *trans*-$[(aryl)Pd^{II}L_2S]^+TfO^-$ (S = solvent) complexes are formed in the oxidative addition of aryl triflates to Pd^0L_4 ($L = PPh_3$) in coordinating solvents such as DMF.[1] Kinetic data on the rate of the oxidative addition have been reported with the following reactivity order: PhI $\gg$ PhOTf $>$ PhBr. The oxidative addition is faster in the presence of chloride ions and leads to neutral *trans*-$(aryl)Pd^{II}ClL_2$ complexes.[1] *trans*-$(aryl)Pd^{II}(OAc)L_2$ complexes are formed when the oxidative addition is performed with the Pd^0 complexes generated from $Pd(OAc)_2$ and PPh_3.[2] When the oxidative addition of aryl triflates is performed in THF with a Pd^0 complex ligated to the bidentate ligand dppf as in $Pd^0(dppf)(\eta^2\text{-}CH_2{=}CHCO_2Me)$, the cationic $[(aryl)Pd^{II}(dppf)]^+$ complexes are not stable at room temperature. However, stable neutral $(aryl)Pd^{II}Cl(dppf)$ and $(aryl)Pd^{II}(OAc)(dppf)$ complexes are formed in the presence of chloride or acetate ions, respectively.[3] Recently, Alcazar-Roman and Hartwig reported kinetic data on the oxidative addition of aryl triflates to $Pd^0(BINAP)_2$ in THF. Stable cationic complexes $[(aryl)Pd(BINAP)(NH_2R)]^+TfO^-$ (R = alkyl) are obtained only in the presence of an amine.[4]

Vinyl triflates are involved in palladium-catalyzed reactions with nucleophiles[5] and, to a lesser extent, with electrophiles.[6] However, chloride ions are always required in coupling reactions of vinyl triflates with organostannanes (Stille reactions), when catalyzed by Pd^0 complexes ligated to PPh_3.[5c−e] A mechanistic investigation of the oxidative addition of vinyl triflates to Pd^0L_4 ($L = PPh_3$), reported by Scott and Stille[5d] in 1986 and reinvestigated by Farina et al.[7] in 1993, revealed that unstable noncharacterized cationic $[(\eta^1\text{-vinyl})Pd^{II}L_n]^+$ (n = 2, 3?) complexes were probably formed in THF, whereas stable, neutral, well-characterized $(\eta^1\text{-vinyl})Pd^{II}ClL_2$ complexes were generated when the oxidative addition was performed in the presence of chloride anions in THF.

Stang et al. have investigated the mechanism of the oxidative addition of vinyl triflates to Pt^0 complexes.[8] With $Pt^0(PPh_3)_2(\eta^2\text{-}CH_2{=}CH_2)$ as the starting material, in the absence of extra phosphine, the reaction proceeds in two steps: a first complexation of the active species Pt^0L_2 to the C=C bond of the vinyl triflate to form $(\eta^2\text{-vinyl-OTf})Pt^0L_2$ complexes (eq 1), followed by a fast intramolecular rearrangement step (in fact, the real oxidative addition step), which gives neutral complexes



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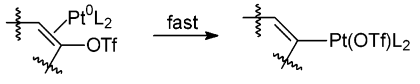

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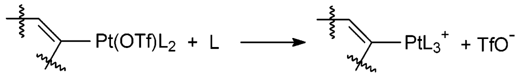

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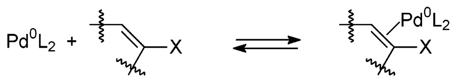
(η^1-vinyl)$Pt^{II}(OTf)L_2$ in toluene (eq 2). Cationic complexes $[(\eta^1\text{-vinyl})Pt^{II}L_3]^+TfO^-$ have been formed from $Pt^0(PPh_3)_4$, i.e., in the presence of extra phosphine (eq 3),[8] and characterized by conductivity measurements in nitromethane. Kinetic data on the oxidative addition of vinyl triflates to $Pt^0(PPh_3)_4$ in toluene have also been reported.[8b] The intermediate (η^2-vinyl-OTf)$Pt^0(PPh_3)_2$ complexes (eq 1) have not been characterized, in contrast to (η^2-vinyl-X)$Pt^0(PPh_3)_2$ complexes (X = Cl, Br).[8b]

The mechanism of the oxidative addition of vinyl halides to Pd^0 complexes ligated by a bisphosphine ligand has been reported by Brown and Cooley.[9] In THF, they have observed, at low temperatures, the reversible formation of intermediate complexes (η^2-vinyl-X)Pd^0L_2 (L_2 = dppf; X = Br, Cl) in the oxidative addition of vinyl halides to (η^2-$CH_2{=}CH_2$)Pd^0L_2 (L_2 = dppf) (eq 4), with subsequent formation of stable (η^1-vinyl)$PdXL_2$ (L_2 = dppf; X = Cl, Br, I) (eq 5).[9] In a qualitative comparison of reactivity, Brown and Cooley have established that the rate of the internal rearrangement (eq 5) is halogen dependent. Indeed, the stability of the intermediate (η^2-vinyl-X)Pd^0(dppf) complex follows the order vinyl chloride > vinyl bromide > vinyl iodide. In other words, the facility of the activation of the C−X bond by the Pd^0 follows the same order as for aryl halides; i.e., C−I > C−Br > C−Cl.[9]



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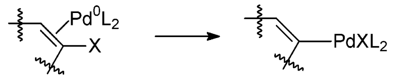

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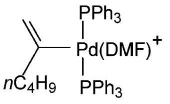
However, kinetic data on the rate of the oxidative addition of vinylic electrophiles with Pd^0 complexes are scarce. Kinetic data on the comparative reactivity of $Pd^0(PPh_3)_4$ with (*Z*)- and (*E*)-β-bromostyrene in DMF are available.[10] The reversibility of the oxidative addition of (*Z*)- and (*E*)-1,2-dichloroethylene to Pd^0 complexes has also been established.[11] To our knowledge, nothing is known on the reactivity of vinyl triflates with Pd^0 complexes. We report herein some results on the kinetics of the oxidative addition of vinyl triflates to $Pd^0(PPh_3)_4$ (which is a catalytic precursor for Stille reactions[5c−g]) and a comparison with that of vinyl bromides in DMF. The cationic complexes *trans*-$[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+TfO^-$ have been characterized.

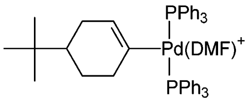
Results and Discussion

Evidence of the Formation of Cationic $[(\eta^1$-vinyl)$Pd(PPh_3)_2(DMF)]^+$ Complexes in the Oxidative Addition of Vinyl Triflates to $Pd^0(PPh_3)_4$ in DMF. Since DMF appears to be a good coordinating solvent for cationic Pd^{II} complexes,[1] the oxidative addition of the vinyl triflate **1a** (Table 1) to $Pd^0(PPh_3)_4$ was performed in DMF and monitored by conductivity measurements to detect ionic species.[12,13] The reaction was performed at 10 °C with 1 equiv of **1a**. The conductivity κ of a solution of $Pd^0(PPh_3)_4$ (2 mM) in DMF (residual conductivity: $\kappa_0 = 3\ \mu S\ cm^{-1}$) increased after addition of 1 equiv of **1a** and reached the limiting value k_{lim}, which was constant within the time scale investigated here (Figure 1a). This establishes that ionic species were formed in a fast reaction ($t_{1/2} = 4$ s) as determined in Figure 1b, which exhibits the very first time of the experiment of Figure 1a. The ionic species were actually generated in the oxidative addition, as attested to by the concomitant disappearance of the Pd^0 complex, monitored independently by amperometry (vide infra) (Figure 1b). The ionic species were stable at 10 °C, beyond the time required for the oxidative addition, as demonstrated by the constant limiting value of the conductivity k_{lim} at the end of the reaction (Figure 1a).

The cationic complex $[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+$ (**3a**$^+$) generated in the oxidative addition of the vinyl triflate **1a** (eq 6) was characterized by electrospray mass spectrometry with its counteranion TfO^-, as was **3b**$^+$ generated from **1b**. The oxidative additions were carried out in DMF and the electrospray analysis performed immediately after mixing and dilution in methanol.



3a$^+$



3b$^+$

Molecular ions at *m*/*z* 713 and 767 were observed for the $[(\eta^1\text{-vinyl})Pd(PPh_3)_2]^+$ cation in complexes **3a**$^+$ and **3b**$^+$, respectively, with the predicted isotope pattern due to the Pd atom. Only two PPh_3 groups were ligated to the Pd^{II} atom.

The cationic complexes **3a**$^+$ and **3b**$^+$ were then characterized by ^1H NMR spectroscopy. The oxidative addition of **1a** (1 equiv) to $Pd^0(PPh_3)_4$ in DMF-d_7 was monitored in an NMR tube. The reaction led to complex **3a**$^+$, for which the vinylic and aliphatic protons were shifted upfield when compared to the protons of **1a** (see Experimental Section). The counteranion TfO^- was also characterized by ^{19}F NMR spectroscopy by comparison with an authentic sample of nBu_4NOTf. The complex **3a**$^+TfO^-$ was the only detectable complex and was stable for at least 30 min at 25 °C. After 2 h, the ^1H NMR spectrum exhibited, besides the signals of **3a**$^+$, a new set of signals in which the protons of the butyl group were located closed to those of the butyl group of **1a**, but two vinylic protons were located at lower field than the two vinylic protons of **1a** (see Experimental Section). This new set of signals which appeared at long times was assigned to the vinylphosphonium salt[14] $[CH_2{=}C(nC_4H_9)\text{-}PPh_3]^+TfO^-$ (**5a**$^+TfO^-$), whose cation was also characterized by electrospray mass spectrometry (*m*/*e* 345). After 17 h, the ratio **3a**$^+$:**5a**$^+$ was equal to 1:0.8, indicating that after 17 h the cationic complex **3a**$^+$ was still the major complex in solution.

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[10] Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1981**, *209*, 109.

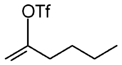
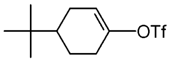
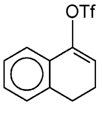
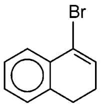
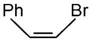
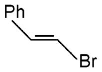
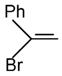
[11] Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 1670.

[12] For the characterization of ionic coordination compounds by conductivity measurements see: Geary, W. J. *Coord. Chem. Rew.* **1971**, *7*, 81.

[13] For the use of conductivity measurements for the characterization of cationic organopalladium(II) complexes and the determination of kinetic data see: Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017.

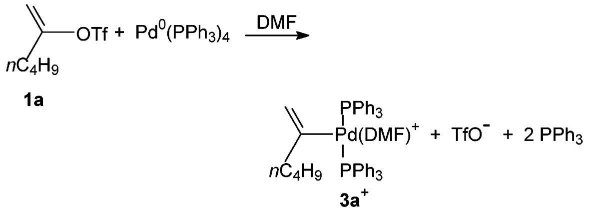
[14] For a related vinylphosphonium salt see ref 16.

Table 1. ^{31}P NMR Shifts[a] of (η^1-vinyl)Pd^{II} Complexes Formed in the Oxidative Addition of Vinyl Triflates or Bromides to Pd^0(PPh$_3$)$_4$ in DMF (L = PPh$_3$)

entry	Vinyl-X	Addend	$[(\eta^1\text{-vinyl})PdL_2(DMF)]^+,X^-$ δ (ppm)	$(\eta^1\text{-vinyl})PdBrL_2$ δ (ppm)
1	 **1a**[b]	none	22.16[c]	-
2	 **1b**[b]	none	22.47	-
3	 **1c**[b]	none	22.66[c]	-
4	**1c**[b]	PPh$_3$ (4 equiv)[d]	22.70	-
5	 **2c**[e]	none	none	23.37[f,g]
6	**2c**[e]	Br$^-$ (10 equiv)[h]	none	23.26[g]
7	 **2g**[e]	none	none	23.20[g]
8	 **2h**[e]	none	20.54 (traces)	24.38[g]
9	 **2i**[e]	none	none	22.87[g]

[a] At 101.2 MHz in DMF containing 10% of acetone-d_6. δ values are referred to H_3PO_4 as external reference. [b] Vinyl-OTf:Pd^0(PPh$_3$)$_4$ = 1:1. [c] Free PPh$_3$ was also detected at −5.27 ppm with an integration close to that of [(η^1-vinyl)Pd(PPh$_3$)$_2$(DMF)]$^+$. [d] Preferably added to Pd^0(PPh$_3$)$_4$. Free PPh$_3$:PPh$_3$ of [(η^1-vinyl)Pd(PPh$_3$)$_2$(DMF)]$^+$ = 3. [e] Vinyl-Br:Pd^0(PPh$_3$)$_4$ = 30:1. [f] Two tiny doublets were observed at δ 29.83 (d, J_{PP} = 33 Hz) and 32.90 (d, J_{PP} = 33 Hz) ppm and assigned to (η^2-**2c**)Pd^0(PPh$_3$)$_2$. [g] Free PPh$_3$ was also detected at −5.30 ppm with an integration close to that of (η^1-vinyl)PdBr(PPh$_3$)$_2$. [h] Added as nBu$_4$NBr to Pd^0(PPh$_3$)$_4$ prior to the addition of **1c** or **2c**.

The oxidative addition of **1a** to Pd^0(PPh$_3$)$_4$ performed under stoichiometric conditions was also monitored by ^{31}P NMR spectroscopy in DMF. Fifty minutes after mixing, the spectrum exhibited one singlet assigned to the cationic complex **3a**$^+$TfO$^-$ (22.1 ppm), the singlet of the vinylphosphonium salt **5a**$^+$TfO$^-$ (24.7 ppm) with the ratio **3a**$^+$:**5a**$^+$ = 1:0.3, and the singlet of the free PPh$_3$ (−5.16 ppm) (eq 6). The presence of a singlet indicates that the two PPh$_3$ ligands of **3a**$^+$ sit in a trans position on the Pd atom. The fourth coordination site is occupied by the DMF. The ^{31}P NMR singlet of the vinylphosphonium species **5a**$^+$ increased with time at the expense of that of complex **3a**$^+$, while the signal of the free PPh$_3$ was no longer detected; instead, a broad signal was found at 3.2 ppm characteristic of Pd^0(PPh$_3$)$_3$ in equilibrium with Pd^0(PPh$_3$)$_2$ and PPh$_3$.[15] Therefore, the Pd^0 complex disappeared and the free PPh$_3$ appeared at short times (oxidative addition, eq 6); then at longer times, the Pd^0 complex appeared again and the free PPh$_3$ disappeared (eq 7).



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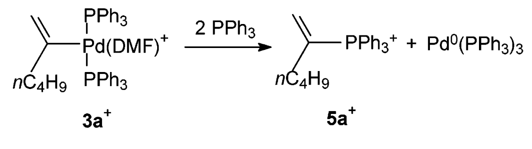

(7)

It is thus established that a fast oxidative addition of a vinyl triflate to Pd^0(PPh$_3$)$_4$ generates the cationic complex [(η^1-vinyl)Pd(PPh$_3$)$_2$(DMF)]$^+$ (eq 6), which slowly decomposes to a vinylphosphonium salt and a Pd^0

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(15) Amatore, C.; Khalil, F.; Jutand, A.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

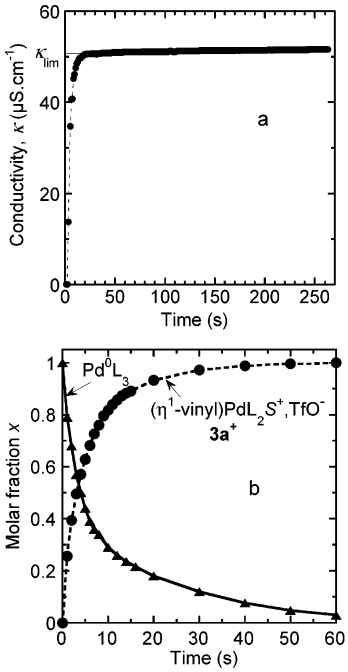
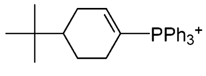


Figure 1. Kinetics of the oxidative addition of CH_2═C(*n*Bu)-OTf (**1a**; 2 mM) to $Pd^0(PPh_3)_4$ (2 mM) in DMF at 10 °C. (a) Kinetics of the formation of $[CH_2$═C(*n*Bu)Pd-$(PPh_3)_2(DMF)]^+TfO^-$ (**3a**$^+$TfO$^-$): variation of the conductivity κ versus time. $\kappa = \kappa_{exp} - \kappa_0$ (κ_{exp} = experimental conductivity at t; κ_0 = initial residual conductivity of 3 μS cm^{-1}). (b) Variation of the molar fraction of $Pd^0(PPh_3)_3$ versus time (—), monitored by amperometry and variation of the molar fraction of the ionic species **3a**$^+$TfO$^-$ versus time (- - -), monitored by conductivity measurements ($0 < t < 60$ s in Figure 1a).

complex (eq 7). The formation of vinylphosphonium salts from PPh_3 and vinyl triflates, catalyzed by Pd^0 complexes, has been reported by Stang et al.[16] It requires excess PPh_3 and refluxing THF. We have now evidence that the vinylphosphonium salt is generated from the cationic complex **3a**$^+$ together with a Pd^0 complex (eq 7), probably by a reductive-elimination step. This Pd^0 complex can only be observed when the oxidative addition is performed under stoichiometric conditions. Indeed, if the vinyl triflate is in excess, the Pd^0 formed together with the vinylphosphonium salt undergoes a second fast oxidative addition with the excess vinyl triflate. As a result, we observe a catalytic transformation of the vinyl triflate to the vinylphosphonium salt, limited by the number of PPh_3 groups delivered by $Pd^0(PPh_3)_4$. Consequently, the stable cationic complex $[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+$, which needs to be stabilized by at least two PPh_3 groups, has little chance of being detected and characterized when the vinyl triflate is in excess, because all the stabilizing PPh_3 ligands will be transformed into the vinylphosphonium salt.

The molar conductivity of **3a**$^+$TfO$^-$ was calculated in DMF at 10 °C: $\Lambda_M = 25\ (\pm 2)$ S cm^2 mol^{-1}. This value is indicative of a 1:1 electrolyte in solution in DMF.[12]

As mentioned above, the complex **3b**$^+$TfO$^-$ formed in the oxidative addition of the vinyl triflate **1b** (1 equiv) to $Pd^0(PPh_3)_4$ was characterized by electrospray mass spectrometry. The cation of the vinylphosphonium salt **5b**$^+$TfO$^-$ was also detected (*m*/*e* 399).



5b$^+$

The oxidative addition was then monitored by ^{1}H NMR in DMF-d_7 under stoichiometric conditions. Fifteen minutes after mixing, the cationic complex **3b**$^+$ was formed in 26% yield and traces of the vinylphosphonium species **5b**$^+$ were already detected.[14] The color of the solution turned progressively from orange to yellow. After 1 h, the three compounds **1b**, **3b**$^+$, and **5b**$^+$ (easily detected by their vinylic protons at 5.92, 5.18, and 6.85, respectively) were present in equal amounts. After 3 h, only the vinylphosphonium species **5b**$^+$ was detected. Therefore, the oxidative addition of **1b** was slower than that **1a** (vide supra, Table 2) and decomposition of **3b**$^+$ to **5b**$^+$ occurred within a similar time scale. The oxidative addition was monitored by ^{31}P NMR spectroscopy in DMF. One hour after mixing, two singlets assigned to **3b**$^+$ (22.66 ppm) and **5b**$^+$ (23.2 ppm) were observed. The free PPh_3 was not detected, but a broad signal was found characteristic of $Pd^0(PPh_3)_n$ complexes[15] generated with the vinylphosphonium salt in a reaction similar to that reported in eq 7.

The complexes $[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+TfO^-$ formed in the stoichiometric oxidative addition of vinyl triflates **1a**−**c** to $Pd^0(PPh_3)_4$ were all characterized in DMF by a ^{31}P NMR singlet (Table 1, entries 1−3), attesting to a trans geometry for the cationic Pd^{II} complex (eq 8). The complex **3c**$^+$TfO$^-$ formed in the oxidative addition of **1c** to $Pd^0(PPh_3)_4$ seems to be the more stable of the series. When the oxidative addition was performed in the presence of 4 equiv of PPh_3, the singlet of **3c**$^+$TfO$^-$ was still observed at short times (Table 1, entries 3 and 4) with a ratio of the free PPh_3 and the ligated PPh_3 equal to 3. This excludes the formation of the three-phosphine-ligated complex $[(\eta^1\text{-vinyl})Pd(PPh_3)_3]^+$ as was the case for analogous platinum complexes (eq 3) in toluene.[8a]

$$Pd^0(PPh_3)_4 + \text{vinyl-OTf} \rightarrow \\ \textit{trans}\text{-}(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)^+ + TfO^- + 2PPh_3 \quad (8)$$

Consequently, in a coordinating solvent such as DMF, cationic *trans*-$[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+$ complexes are generated with TfO$^-$ as the counteranion in the oxidative addition of vinyl triflates to $Pd^0(PPh_3)_4$ (eq 8). However, such complexes are less stable than $[(\text{aryl-}PdL_2(DMF)]^+TfO^-$ complexes.[1] They decompose to the vinylphosphonium salt with formation of Pd^0 complexes. The time scale of this decomposition may be close to that of the oxidative addition.

Formation of Neutral (η^1-vinyl)PdBr(PPh_3)$_2$ Complexes in the Oxidative Addition of Vinyl Bromide to $Pd^0(PPh_3)_4$ in DMF. The oxidative addition of the vinyl bromide **2c** with $Pd^0(PPh_3)_4$ was investigated by ^{31}P NMR spectroscopy in DMF. The neutral *trans*-(η^1-vinyl)PdBr$(PPh_3)_2$ complex **4c** was expected (eq 9), as

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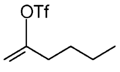
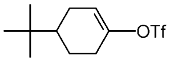
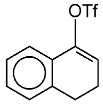
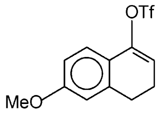
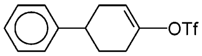
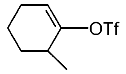
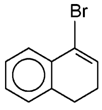
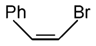
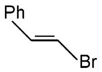
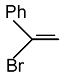
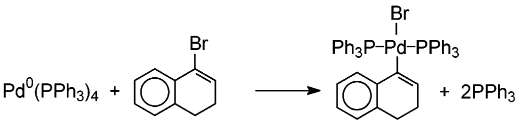
[16] (a) Kowalski, M. H.; Hinkle, R. J.; Stang, P. J. *J. Org. Chem.* **1989**, *54*, 2783. (b) Hinkle, R. J.; Stang, P. J.; Kowalski, M. H. *J. Org. Chem.* **1990**, *55*, 5033.

Table 2. Kinetics of the Oxidative Addition of Vinyl Triflates and Bromides to $Pd^0(PPh_3)_4$ (2 mM) in DMF at 30 °C[a]

Entry	Vinyl-X	addend	$k_XK_1K_2$ (s^{-1})	k_{app} ($M^{-1}s^{-1}$)
1	 **1a**	none	16	5300
2	 **1b**	none	1.6	530
3	**1b**	Cl^- (10 equiv)		600
4	**1b**	Cl^- (200 equiv)		730
5	 **1c**	none	4.6	1530
6	 **1d**	none	9.6	3200
7	 **1e**	none	2.0	660
8	 **1f**	none	0.52	170
9	 **2c**	none	0.0004	0.13
10	 **2g**	none	0.0011	0.37
11	 **2h**	none	0.038	13
12	 **2i**	none	0.091	30

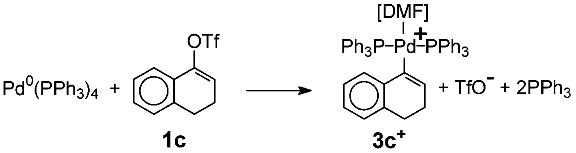
[a] Scheme 1 for X = Br and Scheme 2 for X = OTf.

reported for related vinyl bromides in nondissociative solvents.[10,17]



2c **4c** (9)

Indeed, besides the signal of the free PPh_3, a singlet was observed at 23.37 ppm (Table 1, entry 6) which differed from the singlet of the cationic complex $\mathbf{3c}^+$ (22.66 ppm) formed in the oxidative addition of the vinyl triflate **1c** to $Pd^0(PPh_3)_4$ (eq 10, entry 3 in Table 1).



1c $\mathbf{3c}^+$ (10)

The singlet at 23.37 ppm was not affected by the addition of 10 equiv of bromide ions (Table 1, entry 6). It characterizes the neutral complex **4c** formed in the oxidative addition (eq 9) which, at the NMR concentra-

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(17) (a) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667. (b) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

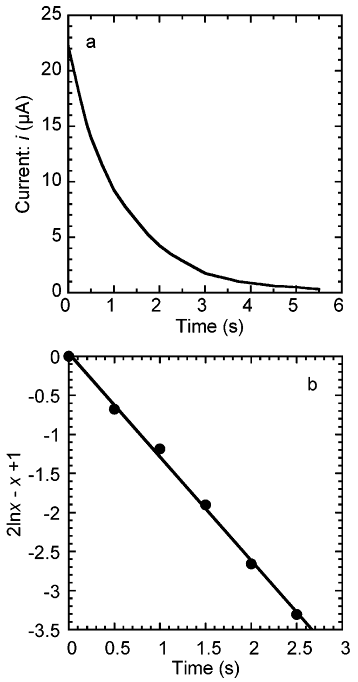
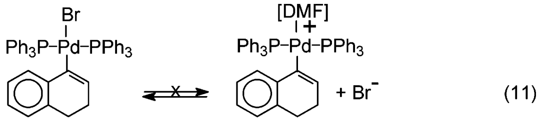


Figure 2. Kinetics of the oxidative addition of (*E*)-β-bromostyrene (**2h**; 70 mM) to $Pd^0(PPh_3)_4$ ($C_0 = 2$ mM) in DMF at 30 °C. (a) Variation versus time of the oxidation current *i* of $Pd^0(PPh_3)_3$ at a rotating gold disk electrode (i.d. 2 mm, $\omega = 105$ rad s^{-1}) polarized at +0.35 V, on the plateau of the oxidation wave of $Pd^0(PPh_3)_3$. (b) Plot of $2 \ln x - x + 1$ versus time ($x = [Pd^0L_3]/[Pd^0L_3]_0 = i/i_0$ with i = oxidation current of Pd^0L_3 at time t, i_0 = initial oxidation current of Pd^0L_3, and L = PPh_3). $2 \ln x - x + 1 = -k_{exp}t$.

tion (16 mM), did not dissociate in DMF to the cationic complex **3c**$^+$ (eq 11).[18]



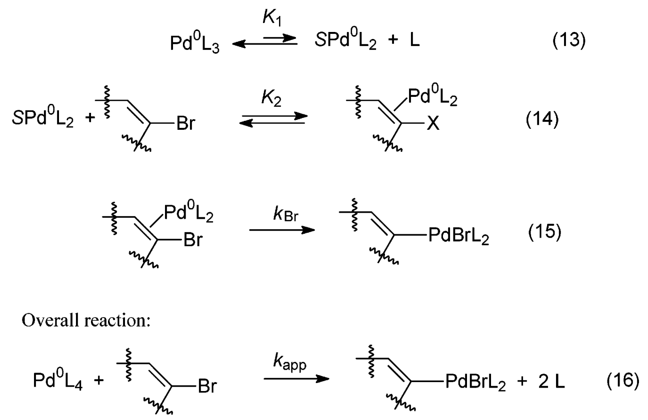
4c **3c**$^+$

The oxidative addition of the vinyl bromides **2g**,**h**[10,17b] and **2i** to $Pd^0(PPh_3)_4$ was also monitored by ^{31}P NMR spectroscopy in DMF at 25 °C. The singlet of the free phosphine was detected together with the singlet of *trans*-(η^1-vinyl)PdBr$(PPh_3)_2$ (eq 12) with similar integration (Table 1).

$$Pd^0(PPh_3)_4 + \text{vinyl-Br} \rightarrow \textit{trans}\text{-}(\eta^1\text{-vinyl})PdBr(PPh_3)_2 + 2PPh_3 \quad (12)$$

Rate of the Oxidative Addition of Vinyl Bromides to $Pd^0(PPh_3)_4$ in DMF. $Pd^0(PPh_3)_4$ ($C_0 = 2$ mM) dissociates in DMF to the major complex $Pd^0(PPh_3)_3$, which then affords $SPd^0(PPh_3)_2$ as the reactive complex in oxidative additions (eq 13).[1,15,19] The kinetics of the oxidative addition of vinyl bromides **2c** and **2g**–**i** with $Pd^0(PPh_3)_4$ was investigated by amperometry at 30 °C. The oxidation peak of $Pd^0(PPh_3)_3$ at +0.06 V vs SCE disappeared after addition of a vinyl bromide. The kinetics of the oxidative addition was then monitored by amperometry at a rotating gold disk electrode polarized at +0.35 V, on the plateau of the oxidation wave of $Pd^0(PPh_3)_3$.[1,19] After addition of the vinyl bromide, the decay of the oxidation current *i* of $Pd^0(PPh_3)_3$ (proportional to its concentration) was recorded versus time (Figure 2a).

Scheme 1. Mechanism of the Oxidative Addition of Vinyl Bromides to $Pd^0(PPh_3)_4$ in DMF



By analogy to related metals and ligands (Pt^0/PPh_3[8b] and Pd^0/dppf[9]), (η^2-vinyl-Br)$Pd^0(PPh_3)_2$ complexes are probably formed as intermediate complexes in the course of the oxidative addition (eq 14). The mechanism of the oxidative addition is then as proposed in Scheme 1.According to Scheme 1, the kinetic law of the overall oxidative addition (eq 16) is given by eq 17.[20a] In the

$$d[Pd^0L_3]/dt = -k_{app}[Pd^0L_3][\text{vinyl-Br}] = -k_{Br}K_1K_2[Pd^0L_3][\text{vinyl-Br}]/[L] \quad (17)$$

presence of excess vinyl bromide (pseudo-first-order conditions) and taking into account the fact that PPh_3 is continuously released in reaction 13 when the oxidative addition proceeds, the integration of eq 17 gives eq 18 ($x = [Pd^0L_3]/[Pd^0L_3]_0 = i/i_0$ with i = oxidation current

$$2 \ln x - x + 1 = -k_{Br}K_1K_2[\text{vinyl-Br}]t/C_0 \quad (18)$$

of Pd^0L_3 at time t and i_0 = initial oxidation current of Pd^0L_3). When the oxidative addition was performed from (*E*)-β-bromostyrene (**2h)**, the plot of $2 \ln x - x + 1$ versus time was linear (Figure 2b): $2 \ln x - x + 1 = -k_{exp}t$. Plotting k_{exp} versus (*E*)-β-bromostyrene (**2h**) concentration afforded a straight line (Figure 3), which confirms that the reaction order in the vinyl bromide is 1 (eq 18). Consequently, $k_{exp} = k_{Br}K_1K_2[\text{vinyl-Br}]/C_0$. The slope of this straight line allows the determination of $k_{Br}K_1K_2$ (s^{-1}) (Table 2), which characterizes the reactivity of the

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[18] In the course of the oxidative addition of **2c** with $Pd^0(PPh_3)_4$, two tiny doublets were also observed at 39.83 and 32.90 ppm (J_{PP} = 33 Hz) together with the singlet of complex **4c**. They may characterize the intermediate complex (η^2-**2c**)$Pd^0(PPh_3)_2$ observed in related oxidative addition of vinyl bromides.[8b,9]

[19] Fauvarque, J. F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *209*, 109.

[20] (a) The expression of the reaction rate is $v = k_1k_2k_X[Pd^0L_3][\text{vinyl-X}]/(k_{-1}k_{-2}[L] + k_{-1}k_X[L] + k_2k_X[\text{vinyl-X}])$. k_1 and k_2 are the forward rate constants and k_{-1} and k_{-2} the backward rate constants of the equilibrium in eq 13 and 14, respectively, and X = Br. Taking into account the fact that the equilibrium in eq 13 is fast and is in favor of Pd^0L_3 ($k_{-1}[L] \gg k_2[\text{vinyl-X}]$), the general equation simplifies into $v = k_1k_2k_X[Pd^0L_3][\text{vinyl-X}]/\{k_{-1}[L](k_{-2} + k_X)\}$, which in turn simplifies to eq 17 (see text) when considering an equilibrium in eq 14 ($k_{-2} \gg k_X$). (b) See ref 20a for the expression of the rate law with X = OTf.

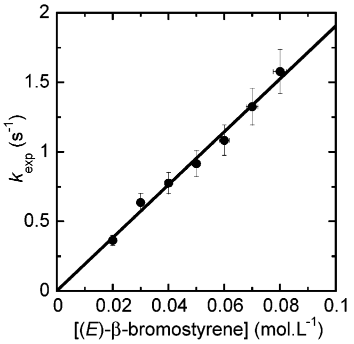
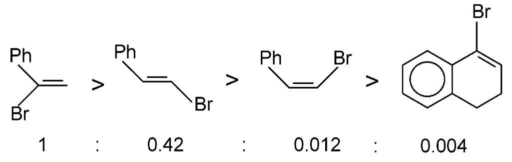


Figure 3. Kinetics of the oxidative addition of (*E*)-β-bromostyrene (**2h**) to $Pd^0(PPh_3)_4$ (C_0 = 2 mM) in DMF at 30 °C. Reaction order in (*E*)-β-bromostyrene: plot of k_{exp} (determined in Figure 2b) versus (*E*)-β-bromostyrene concentration. $k_{exp} = k_{Br}K_1K_2[\text{vinyl-Br}]/C_0$ (Scheme 1).

Chart 1. Relative Reactivity of Vinyl Bromides in Their Oxidative Addition to $Pd^0(PPh_3)_4$ in DMF at 30 °C



vinyl bromide in the oxidative addition to $Pd^0(PPh_3)_4$ in DMF. The value of $k_{app} = k_{Br}K_1K_2/[L]$ (M^{-1} s^{-1}) (eq 16) was also calculated using an average value[21] of [L] = 1.5C_0 (Table 2). However, the fact that the experimental data fit the kinetic law in eq 18 does not prove definitively the existence of the intermediate equilibrium in eq 14. Indeed, were the (η^1-vinyl)$PdBrL_2$ complex directly generated by a reaction of Pd^0L_2 with the vinyl bromide with a rate contant k'_{Br}, the rate law would be $2 \ln x - x + 1 = - k'_{Br}K_1[\text{vinyl-Br}]t/C_0$: i.e., mathematically identical with that expressed in eq 18.[22]

An order of reactivity has been established (Chart 1) for the series of vinyl bromides investigated here (the highest overall rate constant is taken as a reference), evidencing that the oxidative addition is sensitive to steric hindrance: the overall rate constant of the reaction decreases when the steric hindrance increases (compare (*Z*) and (*E*)-β-bromostyrene) and is affected by electronic effects (the most electron rich C=C bond in **2c** is the less reactive one). This is indicative of the complexation of the C=C bond of the vinyl bromide to $Pd^0(PPh_3)_2$ followed by the intramolecular oxidative addition (Scheme 1).

Rate of the Oxidative Addition of Vinyl Triflates to $Pd^0(PPh_3)_4$ in DMF. The oxidative addition of the vinyl triflates **1a** (1 equiv) with $Pd^0(PPh_3)_4$ (C_0 = 2 mM) in DMF was monitored at 10 °C by two analytical techniques. The disappearance of $Pd^0(PPh_3)_4$ in the oxidative addition was monitored by amperometry (Figure 1b), whereas the kinetics of formation of the cationic complex **3a**$^+$TfO$^-$ was monitored by conductivity measurement (Figure 1b). Comparison of the two kinetics shows that the time scale of both reactions was the same. The non-S-shaped form of the kinetic curve featuring the formation of the ionic species (Figure 1b) also indicates that no neutral intermediate complexes, either Pd^0 or neutral Pd^{II} complexes, accumulated in significant amounts in the course of the overall oxidative addition (eq 21). This indicates that, on one hand, the intermediate Pd^0 complex (η^2-vinyl-OTf)$Pd^0(PPh_3)_2$ (eq 19) (if formed) behaved as a transient species which obeys steady-state kinetics. On the other hand, if the intermediate neutral Pd^{II} complex (η^1-vinyl)Pd(OTf)-$(PPh_3)_2$ was formed, its dissociation to (η^1-vinyl)Pd-$(PPh_3)_2(DMF)^+$ and TfO$^-$ would be faster than its rate of formation.

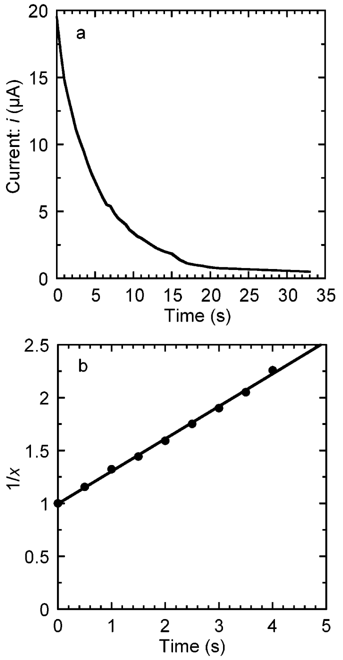


Figure 4. Kinetics of the oxidative addition of the vinyl triflate **1d** (2 mM) to $Pd^0(PPh_3)_4$ (C_0 = 2 mM) in the presence of PPh_3 (60 mM) in DMF at 30 °C. (a) Variation versus time of the oxidation current *i* of $Pd^0(PPh_3)_3$ at a rotating gold disk electrode (i.d. 2 mm, ω = 105 rad s^{-1}) polarized at +0.35 V, on the plateau of the oxidation wave of $Pd^0(PPh_3)_3$. (b) Plot of 1/*x* versus time ($x = [Pd^0L_3]/[Pd^0L_3]_0 = i/i_0$ with *i* = oxidation current of Pd^0L_3 at time *t*, i_0 = initial oxidation current of Pd^0L_3, and L = PPh_3). $1/x = k_{OTf}K_1K_2C_0t/[L] + 1$ (Scheme 2).

The oxidative additions of the vinyl triflates **1a**–**f** investigated here were faster than those performed from vinyl bromides (vide supra). To compare the reactivity of vinyl triflates to that of vinyl halides, which was determined at 30 °C, and to observe reasonable reaction times at 30 °C, the oxidative addition of vinyl triflates was investigated in the presence of 30 equiv of PPh_3, so as to decrease the rate of the overall oxidative addition by shifting the equilibrium in eq 13 toward its left-hand side, i.e. by decreasing the concentration of the active complex $SPd^0(PPh_3)_2$.[19] Under such conditions and using only 1 equiv of the vinyl triflate per $Pd^0(PPh_3)_4$, reasonable time scales were observed (Figure 4a for the oxidative addition of **1d**). The reactions were still fast enough to avoid any interference of the Pd^0 complexes (generated by the decomposition of the cationic complex *trans*-[(η^1-vinyl)$Pd(PPh_3)_2(DMF)]^+$ into the vinylphosphonium salt), which could have under-

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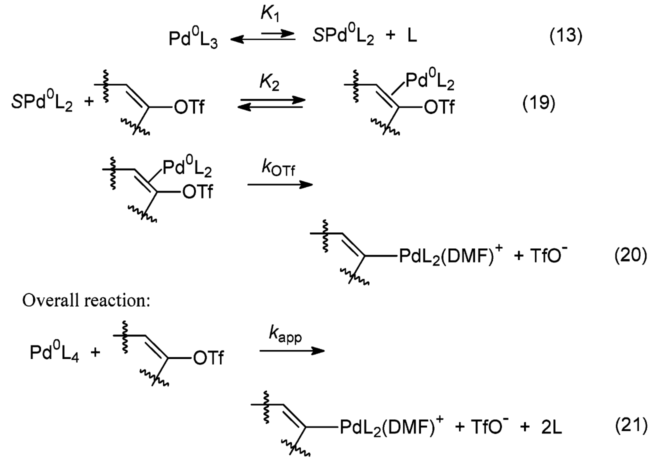
(21) [L] varied from the initial C_0 to 2C_0 at the end of the oxidative addition.

(22) The problematic complexation of the active Pd^0 complex to aryl halides before the oxidative addition step has been discussed in detail by Alcazar-Roman and Hartwig.[4]

Scheme 2. Mechanism of the Oxidative Addition of Vinyl Triflates to $Pd^0(PPh_3)_4$ in DMF



gone a second oxidative addition with the vinyl triflate and disturbed the kinetics.

According to Scheme 2, the kinetic law of the overall oxidative addition (eq 21) is given by eq 22.[20b] In the

$$d[Pd^0L_3]/dt = -k_{app}[Pd^0L_3][\text{vinyl-OTf}] = -k_{OTf}K_1K_2[Pd^0L_3][\text{vinyl-OTf}]/[L] \quad (22)$$

presence of excess PPh_3 and 1 equiv of the vinyl triflate, the disappearance of $Pd^0(PPh_3)_4$ (C_0 = 2 mM) follows the kinetic law of eq 23 ($x = [Pd^0L_3]/[Pd^0L_3]_0 = i/i_0$ with

$$1/x = k_{OTf}K_1K_2C_0t/[L] + 1 \quad (23)$$

i = oxidation current of Pd^0L_3 at time t and i_0 = initial oxidation current of Pd^0L_3, L = PPh_3). The plot of $1/x$ versus time gave a straight line which passed through unity (Figure 4b) in agreement with eq 23 (reaction order in vinyl triflate of 1). $k_{OTf}K_1K_2$ was calculated from the slope (Table 2). With $Pd^0(PPh_3)_4$ (C_0 = 2 mM) as the starting material in the absence of added PPh_3, the apparent rate constant of the overall reaction 21 is $k_{app} = k_{OTf}K_1K_2/[PPh_3]$. The value of the apparent rate constant k_{app} may be then calculated in the absence of added PPh_3 with the average value of $[PPh_3] = 1.5C_0$ (Table 2).[21]

Cyclic vinyl triflates are less reactive than acyclic ones (compare **1a** with **1b**−**f** in Table 2). In the cyclic series, conjugated triflates are more reactive than nonconjugated ones (compare **1c**,**d** with **1b** and **1e**,**f** in Table 2). We have established in a previous work that the oxidative addition of aryl triflates to $Pd^0(PPh_3)_4$ was faster in the presence of added chloride ions.[1] In the case of vinyl triflates, the accelerating effect was still observed but was less significant (entries 2−4 in Table 2) than for aryl triflates.

The vinyl triflates investigated here are considerably more reactive than the vinyl bromides. For **1c** and **2c**, which possess the same vinylic structure, the vinyl triflate **1c** is ca. 10^4 times more reactive than the vinyl bromide **2c** (entries 5 and 9 in Table 2). This is in contrast with the comparable reactivity of PhOTf ($k_{app} = 1.7 \times 10^{-3}$ M^{-1} s^{-1} at 20 °C) and PhBr ($k_{app} = 10^{-3}$ M^{-1} s^{-1} at 20 °C) with $Pd^0(PPh_3)_4$ in DMF.[1] This suggests that the higher reactivity of the vinyl triflate compared to that of vinyl bromide arises from a better complexation of $Pd^0(PPh_3)_2$ with the C=C bond of the vinyl triflate compared to the vinyl bromide.[22]

The vinyl triflates are considerably more reactive than PhOTf ($k_{app} = 1.7 \times 10^{-3}$ M^{-1} s^{-1} in DMF at 20 °C)[1] and even more reactive than PhI (k_{app} = 17 M^{-1} s^{-1} in DMF at 20 °C). The vinyl bromides investigated here are also more reactive than PhBr ($k_{app} = 10^{-3}$ M^{-1} s^{-1} in DMF at 20 °C).[1] The following reactivity orders have been established in DMF:

$$\text{vinyl-OTf} \gg \text{vinyl-Br} > \text{PhBr}$$
$$\text{vinyl-OTf} > \text{PhI} \gg \text{PhOTf} > \text{PhBr}$$

Conclusion

As for aryl triflates, the oxidative addition of vinyl triflates to $Pd^0(PPh_3)_4$ in a coordinating solvent such as DMF gives the cationic complexes *trans*-$[(\eta^1\text{-vinyl})Pd(PPh_3)_2(DMF)]^+TfO^-$. The latter were characterized by conductivity measurements, electrospray mass spectrometry, and NMR spectroscopy when the oxidative addition was performed under stoichiometric conditions. They are less stable than *trans*-$(\text{aryl})Pd(PPh_3)_2(DMF)]^+$-$TfO^-$ (formed in the oxidative addition of aryl triflates to $Pd^0(PPh_3)_4$), since they decompose to phosphonium salt $[\text{vinyl-}PPh_3]^+TfO^-$ and Pd^0 complexes.

The rate constants of the oxidative addition of vinyl triflates and bromides to $Pd^0(PPh_3)_4$ have been determined. Vinyl triflates are considerably more reactive than vinyl bromides. Vinyl triflates are also more reactive than phenyl triflate. Vinyl bromides are more reactive than phenyl bromide.

As already reported, the neutral complexes $(\eta^1\text{-vinyl})$-$PdCl(PPh_3)_2$ were formed when the oxidative addition was performed in the presence of chloride ions.[1,5d] Whereas an accelerating effect of chloride ions on the rate of the oxidative addition of the poorly reactive aryl triflates was observed,[1] the accelerating effect on the highly reactive vinyl triflates is still observed but is very low. Consequently, the positive effect of chloride ions in catalytic Stille reactions involving vinyl triflates and organostannanes[5c−g] does not originate in the oxidative addition, which is probably not rate determining, but rather in bypassing the decomposition of the cationic complex to vinylphosphonium salts by formation of the neutral complexes $(\eta^1\text{-vinyl})PdCl(PPh_3)_2$, as proposed by Scott and Stille.[5d]

Experimental Section

General Methods. All experiments were performed using standard Schlenk techniques under an argon atmosphere. DMF was distilled on CaH_2 and kept under argon. PPh_3 and anhydrous $n$$Bu_4NBr$ were of commercial grade (Aldrich). The vinyl bromides **2h**,**i** were of commercial grade (Aldrich) and used after filtration on alumina. $Pd^0(PPh_3)_4$,[23] the vinyl triflates **1b**−**f**,[24] **1a**,[25] and the vinyl bromides **2c**[26] and **2g**[27] were synthesized according to published procedures.

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The ^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) using H_3PO_4 as an external reference, the ^{1}H NMR spectra on a Bruker spectrometer (250 MHz), and the ^{19}F NMR spectra on a Bruker spectrometer (235 MHz). Cyclic voltammetry and amperometry were performed with a homemade potentiostat and a waveform generator GSTP4 (Radiometer analytical). The current was recorded on a Nicolet 301 oscilloscope. The conductivity was measured with a CDM210 conductivity meter (Radiometer Analytical). The cell constant was 1 cm^{-1}. The conductivity was recorded versus time using a computerized homemade program. Electrospray mass spectrometry was performed on a T100LC spectrometer (JEOL AccuTOF JMS).

General Procedure for ^{31}P NMR Experiments. Into 0.75 mL of DMF were introduced 15 mg (13 μmol) of $Pd^0(PPh_3)_4$ followed by the vinyl triflate **1a** (3 mg, 2 μL, 13 μmol) or the vinyl bromide **2c** (75 mg, 0.39 mmol). A 75 μL amount of acetone-d_6 was then added for the lock. The ^{1}H NMR spectroscopy was performed versus time. In other experiments, bromide ions were introduced as nBu$_4$NBr or PPh_3 when required (see Table 1).

General Procedure for ^{1}H NMR Experiments. Into 0.75 mL of DMF-d_7 were introduced 15 mg (13 μmol) $Pd^0(PPh_3)_4$ followed by the vinyl triflate **1a** (3 mg, 2 μL, 13 μmol). The ^{1}H NMR spectroscopy was performed versus time. ^{19}F NMR experiments were also performed concomitantly.

General Procedure for the Kinetics of the Oxidative Addition Monitored by Amperometry. Experiments were carried out in a three-electrode thermostated cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Radiometer Analytical) separated from the solution by a bridge (3 mL) filled with a 0.3 M nBu$_4$NBF$_4$ solution in DMF. A 12 mL portion of DMF containing 0.3 M nBu$_4$NBF$_4$ was poured into a cell. A 28 mg amount (24 μmol, 2 mM) of $Pd^0(PPh_3)_4$ was then introduced into the cell. The kinetic measurements were performed at a rotating gold disk electrode (i.d. 2 mm, inserted into a Teflon holder, EDI 65109, Radiometer Analytical) with an angular velocity of 105 rad s^{-1} (Radiometer Analytical controvit). The rotating electrode was polarized at +0.35 V on the plateau of the oxidation wave of $Pd^0(PPh_3)_3$. The appropriate amount of the vinyl bromide was then added to the cell and the decay of the oxidation current recorded versus time up to 100% conversion. When the reactivity of vinyl triflates was investigated, 180 mg (0.72 mmol) of PPh_3 was introduced before the vinyl triflate.

General Procedure for the Kinetics of the Oxidative Addition Monitored by Conductivity Measurements. Experiments were carried out in the same thermostated cell as that used for the electrochemical experiments (vide supra). A 28 mg amount (24 μmol, 2 mM) of $Pd^0(PPh_3)_4$ was introduced into the cell containing 12 mL of DMF. The residual conductivity was measured. After addition of 1 equiv of the vinyl triflate **1a** (3.7 μL, 24 μmol, 2 mM), the increase of the conductivity was recorded versus time until a constant final value was obtained corresponding to the end of the oxidative addition.

***trans*-(η^1-vinyl)PdBr(PPh$_3$)$_2$.** The synthesis and characterization of the complexes generated in the oxidative addition of the vinyl bromides **2g**,**h** with $Pd^0(PPh_3)_4$ have been reported.[10,17b]

Vinyl Triflate 1a.[25] ^{1}H NMR (250 MHz, DMF-d_7): δ 0.91 (t, 7.2 Hz, 3 H, CH_3), 1.37 (m, 7.2 Hz, 2 H, CH_2CH_3), 1.52 (m, 7.2 Hz, 2 H, $CH_2CH_2CH_3$), 2.46 (t, 7.2 Hz, 2 H, $=CCH_2CH_2$), 5.25 (d, 4 Hz, 1 H, vinyl *H* trans to OTf), 5.32 (d, 4 Hz, 1 vinyl *H* cis to OTf). ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −74.12 (s).

Complex 3a$^+$TfO$^-$. ^{1}H NMR (250 MHz, DMF-d_7): δ 0.47 (m, 3 H, CH_3), 0.66 (m, 4 H, $CH_2CH_2CH_3$), 1.53 (m, 2 H, $=CCH_2CH_2$), 4.68 (m, 1 H, vinyl *H*), 4.78 (m, 1 H, vinyl *H*), 7.21−7.73 (m, H of PPh_3). ^{31}P NMR (101 MHz, DMF + acetone−d_6 10%): δ 22.1 (s) ppm. ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −77.61 (s). ES MS (DMF/methanol; $C_{42}H_{41}P_2Pd$): *m/z* (%) 713 [M$^+$] (100), 631 [Pd(PPh$_3$)$_2$ + H$^+$], 451 [M$^+$ − PPh$_3$].

Phosphonium Salt 5a$^+$TfO$^-$. ^{1}H NMR (250 MHz, DMF-d_7): δ 0.77 (t, 7.3 Hz, 3 H, CH_3), 1.26 (m, 7.3 Hz, 2 H, CH_2CH_3), 1.51 (m, 7.3 Hz, 2 H, $CH_2CH_2CH_3$), 2.46 (dd, 12 Hz (J_{PH}), 7.3 Hz, 2 H, $=CCH_2CH_2$), 6.20 (dd, 20 Hz (J_{PH}), 4 Hz, 1 H, vinyl *H* trans to PPh$_3^+$), 6.83 (m, 1 H, vinyl *H* cis to PPh$_3^+$), 7.2−7.4 (m, 15 H, aromatic *H*). ^{31}P NMR (101 MHz, DMF + acetone-d_6): δ 24.7 (s). ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −77.61 (s). ES MS (DMF/methanol; $C_{24}H_{26}P$ (345)): *m/z* 345 [M$^+$].

Vinyl Triflate 1b.[24b] ^{1}H NMR (250 MHz, DMF-d_7): δ 0.89 (s, 9 H, CH_3), 1.35 (m, 2 H), 1.98 (m, 2 H), 2.22 (m, 1 H), 2.39 (m, 2 H), 5.92 (t, 3 Hz, 1 H, vinyl H). ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −73.95 (s).

Complex 3b$^+$TfO$^-$. This species was never generated as a pure compound because it started to decompose to the vinylphosphonium salt **5b**$^+$TfO$^-$ before the oxidative addition was over. **3b**$^+$TfO$^-$ was formed in 26% yield with unreacted **1b** at the very beginning of the oxidative addition (15 min after mixing). Due to the complexity of the badly resolved corresponding ^{1}H NMR spectra, only the characteristic signals of **3b**$^+$TfO$^-$ which strongly differ from that of **1b** are presented. ^{1}H NMR (250 MHz, DMF-d_7): δ 0.55 (s, 9 H, H of *t*Bu), 5.18 (m, 1 H, vinyl H). ^{31}P NMR (101 MHz, DMF + acetone-d_6 10%): δ 22.47 (s). ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −77.61 (s). ES MS (DMF/methanol; $C_{46}H_{47}P_2Pd$): *m/z* (%) 767 [M$^+$] (100), 631 [Pd(PPh$_3$)$_2$ + H$^+$], 505 [M$^+$ − PPh$_3$].

Phosphonium Salt 5b$^+$TfO$^-$ (Pure Compound). ^{1}H NMR (250 MHz, DMF-d_7): δ 0.84 (s, 9 H, H of *t*Bu), 1.42 (m, 2 H), 2.02 (m, 1 H), 2.25 (m, 2 H), 2.4 (m, 2 H), 6.85 (br d, 23 Hz (J_{PH}), 1 H, vinyl H), 7.2−7.6 (m, 15 H, aromatic H). ^{31}P NMR (101 MHz, DMF + acetone−d_6): δ 23.2 (s). ^{19}F NMR (235 MHz, DMF + acetone-d_6 10%): δ −77.61 (s). ES MS (DMF/methanol; $C_{28}H_{32}P$): *m/z* 399 [M$^+$].

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