Heterolytic Splitting of Allylic Alcohols with Palladium(0)−TPPTS in Water. Stabilities of the Allylphosphonium Salt of TPPTS and of the Ionic Complex $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$

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The $Pd(TPPTS)_3$ complex (TPPTS is the sodium salt of tris(*m*-sulfophenyl)phosphine) easily ionizes allyl alcohol in water over a wide range of pH: OH^- and TPPTS are released, and $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ is formed. The released TPPTS further reacts with the palladium cationic complex to reversibly produce both the allylphosphonium salt of TPPTS $[(allyl)Ar_3P]^+$ and $Pd(TPPTS)_3$, the latter acting as the catalyst of the allylation of TPPTS by allyl alcohol. Primary allylic alcohols, such as butenol (*trans*-2-buten-1-ol), prenol (3-methyl-2-buten-1-ol), geraniol, and cinnamyl alcohol, react with $Pd(TPPTS)_3$ to produce hydroxide ion, the corresponding hydrosoluble cationic palladium complex, and allylic phosphonium salts. At room temperature, $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ is stable up to pH 12, but beyond this value, palladium precipitates. The temperature has an adverse effect on the complex stability: palladium precipitates at 80 °C, even at pH 7, with the formation of a small amount of propylene. The addition of $[(allyl)Ar_3P]^+$ increases the stability of $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$. Above pH 10, $[(allyl)Ar_3P]^+$ decomposes into OTPPTS and propylene by reaction with OH^-. At lower pH, $[(allyl)Ar_3P]^+$ is slowly isomerized into $[(propenyl)Ar_3P]^+$, which further reduces its stability toward pH and temperature. These consecutive reactions of the TPPTS ligand could explain most of the catalyst instability. This study outlines the basis for a better understanding of the instability phenomenon of the catalytic system Pd(0)−TPPTS in reactions with allylic intermediates, e.g. the Tsuji−Trost reaction, and in the reaction of dienes in aqueous media in which palladium often precipitates.

Introduction

The sodium salt of tris(*m*-sulfophenyl)phosphine (TPPTS) (Figure 1) was first synthesized 30 years ago.[1] Its strong ability to coordinate low-valent transition metals (Co, Ni, Ru, Rh, Pd, and Pt) as strictly nonextractable coordination complexes opened the field of aqueous biphasic catalytic reactions.[2] In 1984, the development of a commercial biphasic oxo synthesis with rhodium TPPTS catalyst (Ruhrchemie/Rhône-Poulenc process) demonstrated the strong potential of this concept.[3] On the laboratory scale, this system fully matched the conditions that allowed a development study: i.e., yield, selectivity, catalyst separation by decantation, and very good stability for 150 h with an excess of TPPTS.[4] This stability was later improved in the Ruhrchemie pilot plant[5] and then in the first industrial unit.[6]

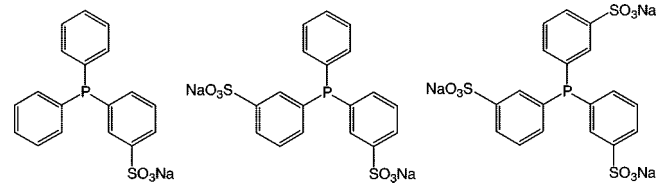

Figure 1. TPPMS, TPPDS, and TPPTS.

Before 1984,[7] palladium catalysts based on the hydrosoluble phosphines TPPTS, TPPDS, and TPPMS (Figure 1) were mainly studied for the dimerization, functionalization, or telomerization of dienes, such as butadiene and isoprene. An important objective was the hydrodimerization of butadiene catalyzed by palladium(0)−TPPTS to produce octadienol (eq 1),[7a] an inter-

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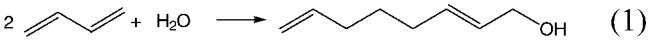
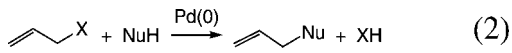
mediate for octanol and C_9 compounds (linear diacid, diamine, and dialcohol). However, the Pd(0) TPPTS catalyst was not stable at 80 °C: a precipitation of metallic palladium occurred after only a few hours of reaction. The exact reasons for such a precipitation are still not well understood. Studies on the hydrodimerization of butadiene were unsuccessfully carried out under similar conditions with various cocatalysts.[8]



(1)

However, the introduction of an excess of the allylic phosphonium salts of TPPMS in the presence of palladium[9] led to a reaction rate and a stability of the catalytic system good enough for the implementation of a commercial process for the production of octadienol (5000 tons/year). Unfortunately, the complexity of the process is likely to limit its potential applications.[10]

A second important reaction was the Tsuji−Trost Pd(0)-catalyzed nucleophilic substitution of allylic compounds, a well-established methodology in organic synthesis (eq 2).[11] However, it was shown only in 1989 that a catalytic allylation could be performed in a two-phase system—water/organic solvent—using water-soluble Pd complexes with catalyst separation.[12] Allylation in a two-phase system was then extended to a variety of nucleophiles using mainly TPPTS and TPPMS ligands with allylic acetates, carbonates, ethers, and chlorides.[13] The instability of the catalyst has already been highlighted.[12,14]



(2)

Allylic alcohols—more available than their derivatives[23]—were directly used in a two-phase system with palladium for the allylation of aromatic amines,[15] for the isoprenylation of an amino acid (4-bromotryptophan) with 1,1-dimethylallyl alcohol,[16] for the C-allylation of phenol or guaiacol,[17] and more recently for the allylation of β-diketones, amines, ethyl acetoacetate,[18] arenethiols,[19] and lactones[20] and for the isoprenylation of haloanilines with 1,1-dimethylallyl alcohol.[21] The allylation of aldehydes was also achieved with allylic alcohols with an indium-promoted palladium−TPPTS catalyst.[22] The allylation of arenethiols was carried out at room temperature with the recycling of the catalyst without an accumulation of byproduct or a loss of catalytic activity.[19] The use of an allylic alcohol as starting material—more easily available than the corresponding ester or carbonate—and the formation of water as the only byproduct make this procedure highly interesting for green chemistry.[23]

Oshima reported that $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ species and TPPTS oxide were readily formed from a mixture of allyl alcohol, palladium acetate, TPPTS, and sodium carbonate.[18] $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ was also formed from palladium allyl chloride dimer and TPPTS in D_2O. We also observed that $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ was formed from the allyl alcohol reaction with the $Pd(TPPTS)_3$ complex at pH 7.2. Moreover, the allylphosphonium salt of TPPTS was stoichiometrically produced in this reaction.[24]

In our study of the C-allylation of phenols by allyl alcohol, we observed that palladium precipitation occurred in basic medium at 80 °C (pH 9.5−12),[24] conditions slightly different from those of the hydrodimerization of butadiene into octadienol in the presence of sodium hydrogenocarbonate and the Pd−TPPTS catalyst.[7a] Recently, the deactivation of a homogeneous Pd catalyst in organic solvent was studied using various Pd(1,1-dimethylallyl)(P-P ligand)OTf complexes as catalytic intermediates and piperidine as nucleophile.[25] The formation of inactive Pd dimers and trimers, a possible first step in the deactivation process of the Tsuji−Trost reaction, led to larger palladium clusters and eventually palladium black. Therefore, it seemed crucial to determine the conditions for the formation of (π-allyl)palladium(II) complexes and phosphonium salts in aqueous solution and their stability versus pH and temperature in order to understand the reasons for the instability of the catalytic system.

We report herein the allylation of $Pd(TPPTS)_3$ with allylic alcohols in water into the ionic compounds $[Pd(\eta^3\text{-alkenyl})(TPPTS)_2]^+$ and the allylic phosphonium salts of TPPTS.[26] The study of the stability—versus pH and temperature—of ionic compounds obtained from allyl alcohol was carried out and

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(26) (a) Homologous $Pt(\eta^3\text{-allyl})(TPPTS)^{2+}$ was recently prepared from $PtCl_2(TPPTS)_2$ and allyl alcohol with stoichiometric formation of 1-hydroxyacetone.[26b] We have shown that $PtCl_2(TPPTS)_2$ catalyzes a selective C-allylation of guaiacol with allyl alcohol into *p*-eugenol and *o*-eugenol (65/35) in water.[26c] The selectivity of the $PtCl_2(TPPTS)_2$ catalyst in this allylation was similar to that obtained with the palladium(0) TPPTS catalyst.[24]. (b) Helfer, D. S.; Phaho, D. S.; Atwood, J. D. *Organometallics* **2005**, *17*, 78–89. (c) Reference 17, patent example number 17.

provided essential results for a better understanding of catalytic reactions in water with palladium and TPPTS.

Results and Discussion

1. Pd(TPPTS)$_3$ Reaction with Allyl Alcohol. Pd(TPPTS)$_3$ was prepared in aqueous solution by the reduction of palladium acetate by an excess of TPPTS, made easier by NaOH addition (TPPTS/Pd molar ratio of 4 or greater) (eq 3).[27,28] By convention, **4** refers to a solution of the Pd(TPPTS)$_3$ complex with either a small excess or no excess of TPPTS and with sodium acetate and TPPTS oxide. **1a**−**3a** refer to [Pd(η^3-allyl)(TPPTS)$_2$]$^+$, TPPTS oxide, and the allylphosphonium salt of TPPTS, respectively.

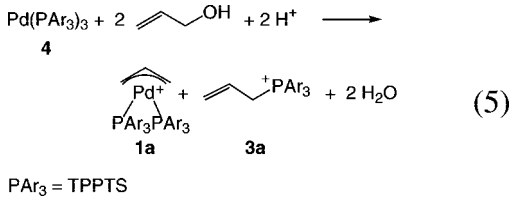
$$\mathrm{Pd(OAc)_2 + 4PAr_3 + 2NaOH \rightarrow Pd(PAr_3)_3 + \underset{\mathbf{2a}}{OPAr_3} + 2NaOAc + H_2O} \qquad \mathrm{PAr_3 = TPPTS} \quad (3)$$

The ^{31}P NMR spectrum of a solution of **4** shows only two signals corresponding to **2a** (δ 35.14 ppm) and **4** (δ 23.85 ppm). However, as previously described,[29] a signal shift toward low-field values was observed for **4** in the presence of an excess of TPPTS due to an exchange reaction of TPPTS with the complex.[30]

We did not observe the dissociation of Pd(TPPTS)$_3$ into Pd(TPPTS)$_2$ and TPPTS in dilute medium by ^{31}P NMR (eq 4; palladium concentrations 2×10^{-4} and 1.2×10^{-4} M): the signal was still close to 23.85 ppm (23.90 and 23.84 ppm, respectively) in the absence of free TPPTS.[31] The Pd(0) TPPTS system can then mainly be considered as Pd(TPPTS)$_3$ with an eventual excess of phosphine (for $n \geq 3$ in this study).

$$\mathrm{Pd(TPPTS)_3 \rightleftharpoons Pd(TPPTS)_2 + TPPTS} \quad (4)$$

a. Reaction at pH 7. As shown previously by us,[24] **4** reacts with allyl alcohol according to eq 5.



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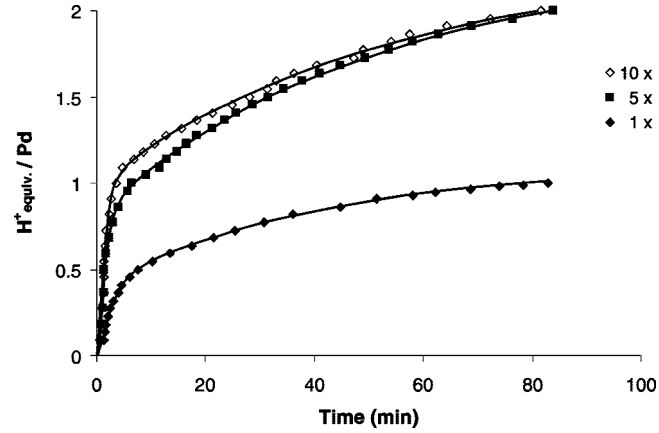

Figure 2. Reaction rate between allyl alcohol and Pd(TPPTS)$_3$: H$^+$/Pd ratio versus time (allyl alcohol/Pd = 10, 5, 1). Conditions: [Pd] initial concentration 0.0055 M in water at room temperature, initial pH 7; after allyl alcohol addition, 0.2 M $HClO_4$ was added to keep the pH at 7.

This reaction consumes protons, which allows a kinetic study by keeping the pH at a constant value by the addition of perchloric acid. Figure 2 shows the curves obtained at room temperature and pH 7 for allyl alcohol/Pd molar ratios of 10, 5, and 1. In the first two cases, the conversion of **4** into palladium allyl complex **1a** and phosphonium species **3a** is quantitative, as observed by ^{31}P NMR. The intensity ratio of the two signals (2/1) is in agreement with eq 5. At pH 7 with an allyl alcohol/Pd molar ratio of 10, Pd(TPPTS)$_3$ prepared with sulfate or chloride exhibited the same reaction rate during the whole reaction.[28] With an excess of allyl alcohol, the curves of Figure 2 show unambiguously that the reaction proceeds in two steps: the proton consumption is very fast for the first few minutes of the reaction and then becomes slower.

With allyl alcohol as limiting reagent, for example allyl alcohol/Pd = 1, the reaction was slower. After 5 h, the amount of acid added corresponds to the amount of allyl alcohol added: the allyl alcohol reacted quasi-quantitatively and was converted into **1a** (60%) and **3a** (40%). The signal of **4** broadened and shifted to lower chemical shifts, indicating the presence of free TPPTS in the solution.

Under similar conditions with various allyl alcohol/palladium ratios lower than 2, the amount of acid added is at least 95% of the amount of allyl alcohol introduced in all cases. Allyl alcohol then reacted quasi-quantitatively. All attempts to detect free alcohol in the reaction medium by ^{1}H NMR failed, which agrees with the above assumption (the detection limit was estimated at ca. 5×10^{-4} M). With a small excess of allyl alcohol (a ratio of 2.09), both **1a** and **3a** are produced quantitatively (see the Supporting Information, reaction of Pd(TPPTS)$_3$ with allyl alcohol as limiting reagent).

b. Reaction at pH 3, 7, and 9. Allylation was performed at pH 3, 7, and 9 (Figure 3). At pH 3 and 7, the initial rate was fast. At pH 3, one proton was consumed per Pd in 1 min, while ca. 5 min is necessary at pH 7, but after 70−80 min the overall reaction was complete. At pH 9, the reaction becomes very slow: one proton was consumed per Pd in 2 h, and the rapid and slow steps cannot be discriminated. These data combined with those

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(28) Pd(TPPTS)$_3$ solutions with sulfate (sulfate/Pd molar ratio 1) were prepared from palladium sulfate according to ref 27a and Pd(TPPTS)$_3$ solutions with chloride (chloride/Pd molar ratio 4) from potassium tetrachloropalladate(II) by the same method.

(29) Choplin, A.; Dos Santos, S.; Quignard, F.; Sigismondi, S.; Sinou, D. *Catal. Today* **1998**, *42*, 471–478.

(30) With a Pd concentration of 0.011 M, the following values were obtained: n (TPPTS/Pd(0) ratio) = 3, δ 23.85 ppm; n = 3.53, δ 21.75 ppm; n = 4.06, δ 17.97 ppm; n = 8, δ 2.06 ppm (TPPTS alone: δ −5 ppm). This variation allows an estimation of the ratio TPPTS/Pd(0) in the solution, even during catalysis. Indeed, under some conditions, the allylation reaction of **4** liberates TPPTS, which will be in equilibrium with the unreacted complex. The chemical shift value of **4** will then allow an estimation of the TPPTS/complex ratio in the solution.

(31) This result involves an equilibrium constant of dissociation K lower than 10^{-5}. It is in agreement with recent results of the dissociation of Pd(TPP)$_3$ (TPP = triphenylphosphine) into TPP and Pd(TPP)$_2$. The dissociation constant was found to be 1.7×10^{-4} in organic medium: Amatore, C.; Jutand, A.; Mensah, L.; Meyer, G.; Fiaud, J.; Legros, J. *Eur. J. Org. Chem.* **2006**, 1185–1192.

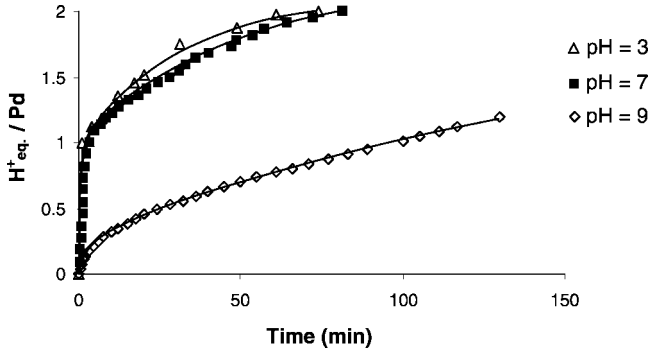
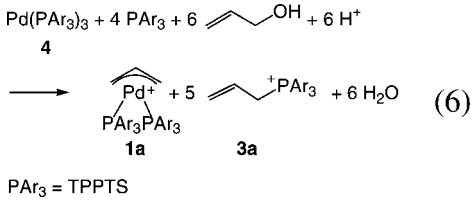


Figure 3. Rate of allyl alcohol reaction with $Pd(TPPTS)_3$: H^+/Pd ratio versus time at pH 3, 7, and 9 at room temperature. Conditions: [Pd] initial concentration 0.0055 M in water at room temperature, allyl alcohol/Pd = 10.

above are in agreement with a pH-dependent formation of **1a** from **4** and a slower but pH-independent formation of **3a** from TPPTS released during the first reaction.

c. Reaction with an Excess of TPPTS .[32,33] The above data show that the transformation of TPPTS into **3a** is catalyzed by palladium species present in the reaction medium. This point can be proven by doing the reaction in the presence of an excess of TPPTS.

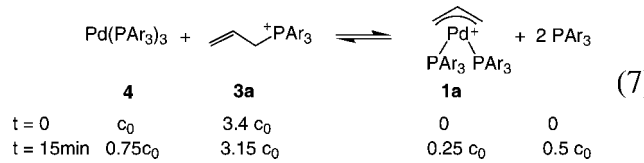
When allyl alcohol and TPPTS were in excess to palladium (allyl alcohol/Pd(0) ≈ 11 and TPPTS/Pd(0) = 7), all palladium was converted into $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ and all the remaining TPPTS molecules were also transformed into phosphonium species **3a**. The addition of 6 H^+ per Pd was necessary to maintain the pH at 7, in agreement with eq 6.



(6)

The initial reaction rate at pH 7 was about 15 times less than that without a TPPTS excess. Similar results obtained in nonaqueous medium also showed a decrease of the reaction rate in the presence of an excess of triphenylphosphine in the Heck reaction with palladium catalyst.[34] A possible explanation for this feature is that TPPTS and the allyl alcohol compete to generate $Pd(TPPTS)_3$ and $Pd(TPPTS)_2$(allyl alcohol), respectively. This latter complex leads to cation **1a** and OH^- by ionization.

d. Reversibility of the Formation of the Allylphosphonium Salt of TPPTS and Ionic Character of the Palladium Complex. The allylphosphonium salt **3a** reacted quickly with complex **4** in solution at room temperature. After the addition of **4** to a solution of **3a,** ^{31}P NMR spectroscopy showed that **4** was partially but rapidly converted into **1a** (conversion 25%). The equilibrium was reached after 20 min (eq 7). Therefore, after the reaction, the concentration of **4** is $0.75c_0$ and that of free TPPTS $0.5c_0$: i.e., the total ratio TPPTS/Pd(0) is 3.66, in agreement with the signal at δ 19 ppm of the ^{31}P NMR spectrum attributed to complex **4** in the presence of a TPPTS excess.



(7)

This reaction can be regarded as a redox reaction between four components, including two ions. The phosphonium ion is reduced into phosphine by the palladium(0) complex, which is transformed into palladium(II) ion.

From the solution containing both **1a** and **3a**, it has not been possible to identify signals from mass spectroscopy that could establish the ionic character of **1a**. The TPPTS, TPPDS, and TPPMS ligands have already been investigated by ESMS in the negative-ion mode and exhibited strong negative ions.[35]

The three homologous Pd(II) complexes of TPPTS (**1a**), TPPDS (**1b**), and TPPMS (**1c**) were prepared by the dissolution of $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ in a well-stirred solution of TPPTS, TPPDS, or TPPMS in water or in D_2O, with a P/Pd atomic ratio of 2 (eq 8) (Supporting Information).[36]

(8)

The ionic character of the complexes was established by electrospray mass spectroscopy (ESMS). The complexes **1a**−**c**, using 10^{-3} M water solutions diluted (1/100) with a mixture of methanol, dichloromethane, and water (v/v 40, 45, 15) containing 0.1% of formic acid, also exhibited ions in their negative form: one major ion with **1c** and three major ions with **1b**. The complex **1a** did not exhibit major ions but many signals. Only two ions in their negative form at *m/z* 1170.7 and 1148.7 were identified (Figure 4). The ion mass spectra exhibited an isotopic

(32) In organic solvent, allylic triphenylphosphonium salt syntheses have been reported from the reaction of TPP with allylic acetates[32a] or allylic trifluoroacetates[32b] in the presence of $Pd(TPP)_4$ catalyst: (a) Tsukahara, Y.; Kinoshita, H.; Inomata, K.; Kotake, H *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3013–3014. (b) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858–6863.

(33) More recently, alkenyl and alkyltriphenylphosphonium salts (RP^+Ph_3, X^-) were prepared from different metal-catalyzed additions of triphenylphosphine and strong acids to alkynes,[33a] 1,3-alkadienes,[33b] and 1-alkenes.[33c] Addition on alkynes with methanesulfonic acid with $LiPF_6$, $X = PF_6^-$, catalyst $Pd(TPP)_4$ or $[RhCl(cod)]_2$: (a) Arisawa, M.; Yamamuchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387–2388. Addition on 1,3-alkadienes with trifluoromethanesulfonic acid, $X = CF_3SO_3$, catalyst $RhH(TPP)_4$: (b) Arisawa, M.; Momozuka, R. *Chem. Lett.* **2002**, 272–73. Addition on alkenes with bis(trifluoromethanesulfonyl)imide (Tf_2NH), $X = (CF_3SO_2)_2N^-$, catalyst $Pd_2(dba)_3$, $CHCl_3$: (c) Arisawa, M; Yamamuchi, M. *J. Am. Chem. Soc.* **2006**, *128*, 272–273.

(34) Amatore, C.; Blart, E.; Genêt, J. P.; Jutand, A.; Lemaire-Audoire, S.; Savignac, M. *J. Org. Chem.* **1995**, *60*, 6829–6839.

(35) Henderson, W.; Olsen, G. M. *Polyhedron* **1998**, *17* (4), 577–588.

(36) When the ratio TPPTS/Pd was increased to 2.25 in the above preparation of **1a**, the compounds **1a**, **4**, and **3a** appeared in the molar ratio **1a/4/3a** = 89/11/11, which showed that TPPTS in excess was partially allylated by **1a**. **4** appeared at 23.26 ppm (normally at 23.85 ppm but TPPTS in excess made a shift of −0.59 ppm). A similar reaction in organic solvent was already observed with allylpalladium chloride dimer and triphenylphosphine (TPP). In the presence of more than 2 equiv of TPP in methanol, allyltriphenylphosphonium cation and palladium(0) TPP complex were formed.[36a] An analogous reaction was observed in DMF without TPP excess because the palladium(0) complex was stabilized with chloride anion and one TPP molecule:[36b] (a) Shaw, B. L.; Powel, J *J. Chem. Soc. A* **1968**, 774–777. (b) Amatore, C.; Jutand, A.; M'Barki, M. A.; Meyer, G.; Mottier, L. *Chem. Eur. J.* **1999**, *5*, 466–473. (c) Amatore, C.; Jutand, A.; M'Barki, M. A.; Meyer, G.; Mottier, L. *Eur. J. Inorg. Chem.* **2001**, 873–880.

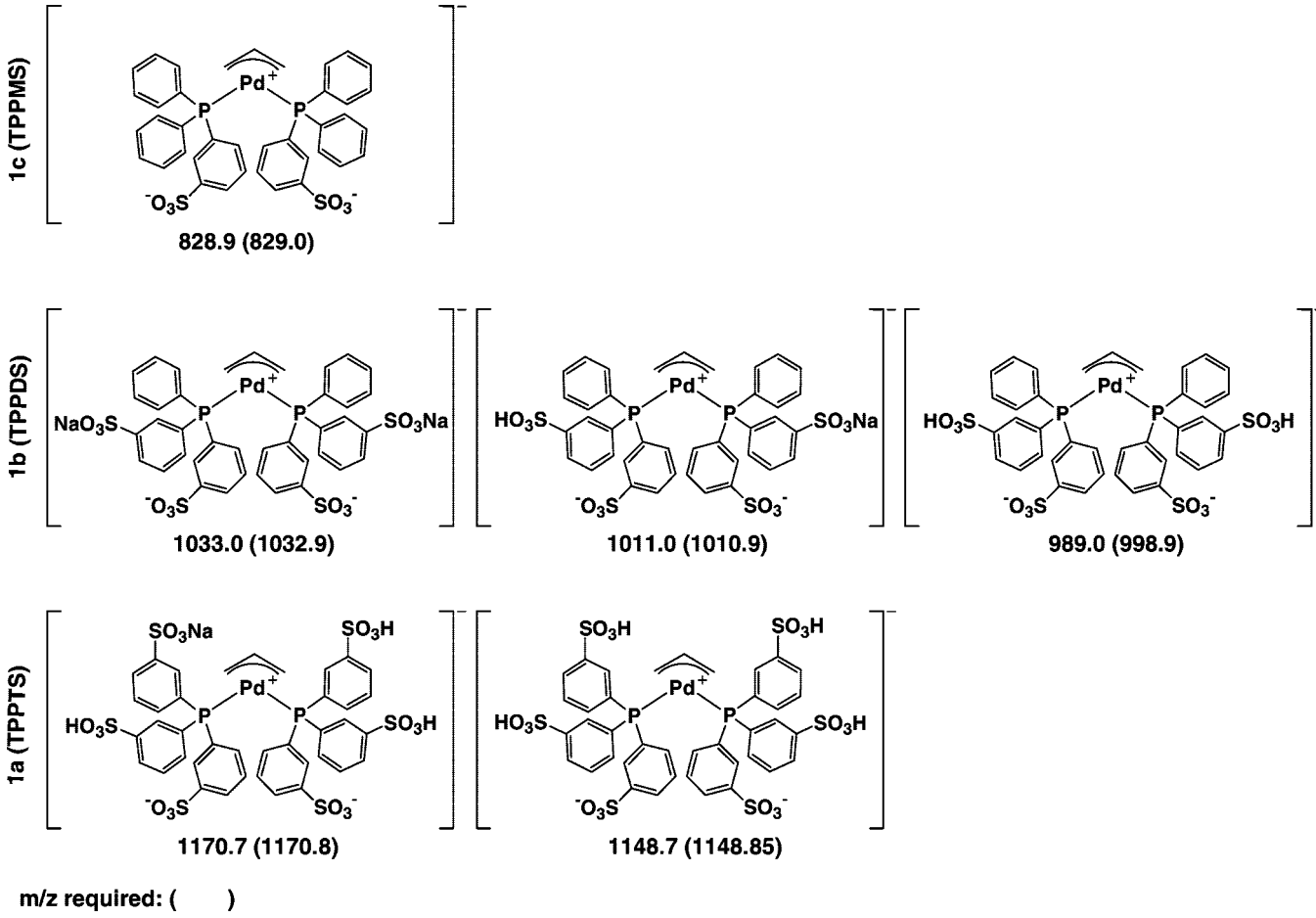


Figure 4. Selected negative-ion electrospray mass spectral data of ionic complexes **1c** (TPPMS), **1b** (TPPDS), and **1a** (TPPTS).

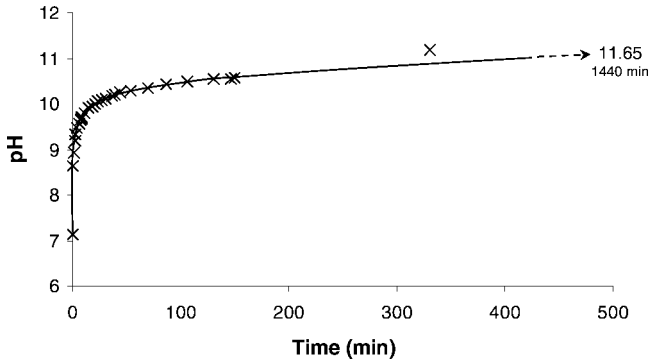
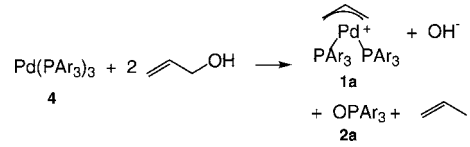


Figure 5. Allyl alcohol reaction without acid addition: pH versus time. Conditions: [Pd] = 0.0055 M in water at room temperature, allyl alcohol/Pd molar ratio 10, initial pH 7.14, final pH 11.65, close to the theoretical pH 11.74, after reaction [OH^-] = [Pd] = 0.0055 M.

pattern that confirms the ionic character of these palladium complexes in solution (see the Supporting Information: mass spectra, NMR data).

e. Allylation with Allyl Alcohol without Acid Addition. Under conditions similar to those above, but without acid addition, the pH increased to basic values after allyl alcohol addition (Figure 5). After 2 h of reaction, the ^{31}P NMR showed that the conversion of **4** was 15% into **1a** and 4% into **3a** (molar ratio **3a**/initial **4**). One day later, the pH of the solution was 11.65, which corresponds to the formation of one hydroxide ion per palladium. Moreover, ^{31}P NMR showed that the conversion of **4** was 100% into **1a**. **3a** was not detected, but the amount of TPPTS oxide **2a** in the solution had increased (**2a**/Pd molar ratio of 1), and propylene was detected in the gas phase. All these data are in agreement with eq 9.



(9)

Starting from pH 11 under the same conditions, the pH was 11.76 after 2 days (theoretical pH 11.81). The conversion of **4** was 100% into **1a**. **3a** was not detected. The amount of TPPTS oxide **2a** in the solution had increased, but a new oxide appeared: the disodium salt of propenylbis(*m*-sulfophenyl)phosphine oxide (**2b**) with the ratio **2b**/**2a** = 23/77.

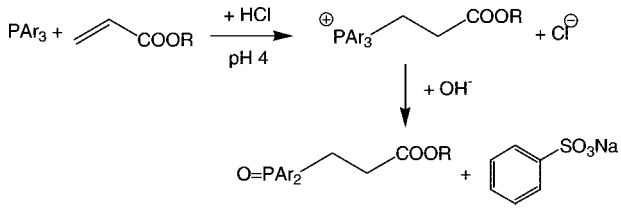
Thus, the lack of **3a** in the synthesis of **1a** from allyl alcohol, palladium acetate, TPPTS, and sodium carbonate, as previously published by Oshima,[18] can be explained by its instability in basic medium.

The instability of hydrosoluble alkyl- and vinyl-substituted triphenylphosphonium salts in basic medium has already been described. The reaction of hydroxide ions with hydrosoluble alkylphosphonium salts derived from TPPTS and ethyl acrylate were reported to lead to a phosphine oxide (Scheme 1).[37] It

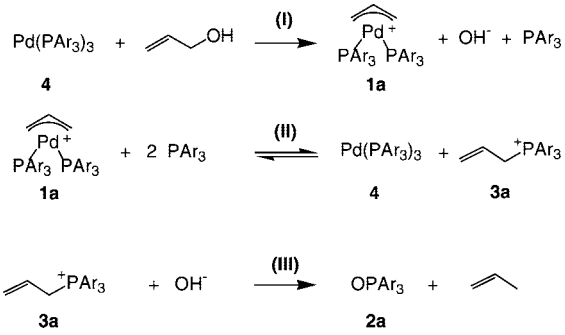
(37) (a) Larpent, C.; Patin, H. *C. R. Acad. Sci. Paris* **1987**, 1055. (b) Larpent, C.; Patin, H. *Tetrahedron* **1988**, *44*, 6107–6118.

(38) (a) Fenton, G. W.; Ingold, C. K. *J. Chem. Soc.* **1929**, 2342. (b) Grayson, M.; Keough, T. P. *J. Am. Chem. Soc.* **1960**, *82*, 3919–3924.

Scheme 1



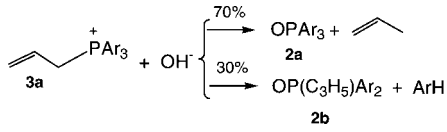
Scheme 2



has long been known that phosphonium salts are decomposed by base to produce tertiary phosphine oxides and hydrocarbons.[38]

Vinyl-substituted triphenylphosphonium salts have already been prepared from TPPTS or TPPMS and various α-acetylenic carboxylic acids. These salts are easily transformed into TPPTS oxide, TPPMS oxide, or vinyl-substituted diphenylphosphine oxide by NaOH addition.[39]

In our case, the addition of sodium hydroxide to a solution of **3a** (0.02 M) at room temperature produced mainly **2a** + propylene (70%) and **2b** (30%). The phosphonium salt decomposition consumed hydroxide ions according to the reaction shown by eq 10.



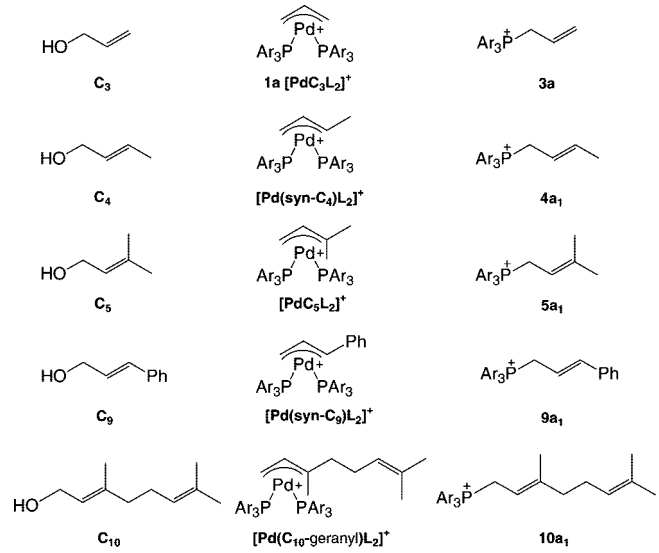
(10)

Unfortunately, palladium appears as a catalyst for the oxidation of TPPTS into TPPTS oxide by allyl alcohol which is mainly reduced into propylene in basic medium. The study of the stability of **3a** solutions without palladium revealed the existence of several transformation reactions of **3a** (see section 3).

f. Overall Mechanism. The first reaction observed between allyl alcohol and $Pd(TPPTS)_3$ was the formation of the complex $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ and the release of a TPPTS molecule and OH^- (Scheme 2, reaction I). This reaction was fast in acidic medium, but its rate decreased greatly around pH 9−10. The initial reaction rate was lower in the presence of an excess of TPPTS. The equilibrium between $Pd(TPPTS)_3$ and $Pd(TPPTS)_2$ could not be demonstrated, but TPPTS and allyl alcohol would be in competition to form the complex $Pd(TPPTS)_2$(allyl alcohol), which would then ionize into OH^- and $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$. TPPTS, the most active nucleophile in the aqueous solution, reacts then with $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ to produce reversibly the allylphosphonium TPPTS species and $Pd(TPPTS)_2$ immediately stabilized into $Pd(TPPTS)_3$ by a second TPPTS molecule (reaction II). By using allyl alcohol as the limiting reagent compared to $Pd(TPPTS)_3$, a high conversion rate of allyl alcohol into $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ and $[(allyl)Ar_3P]^+$ was observed. There are reversible reactions between the four phosphorus compounds, since it was shown that $[(allyl)Ar_3P]^+$ quickly transforms $Pd(TPPTS)_3$ into $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ and 2 TPPTS. In the presence of an excess of allyl alcohol, $Pd(TPPTS)_3$ and the eventual TPPTS in excess are fully transformed into $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ and $[(allyl)Ar_3P]^+$. Palladium finally acts as a catalyst for the transformation of TPPTS into phosphonium hydroxide by the action of allylic alcohol. Under our conditions, this hydroxide is neutralized by an acid during the reaction.

At a nonregulated pH, the reaction releases OH^- and the reversibility of reaction I could be evaluated by the possible measure of an equilibrium for a high pH. However, the instability of phosphonium ions above pH 10 made the system irreversible and therefore removed any equilibrium measure. The allyl alcohol added to the aqueous solution of $Pd(TPPTS)_3$ at a neutral pH transforms it fully into $[Pd(\eta^3\text{-allyl})(TPPTS)_2]^+$ with a pH increase to 11.65 corresponding to 1 OH^- produced by palladium. At the same time, TPPTS is transformed into $[(allyl)Ar_3P]^+$ by producing 1 OH^- and then mainly into OTPPTS and propylene by consuming 1 OH^- (reaction III). Palladium then looks like a catalyst for the oxidation of TPPTS into TPPTS oxide, whereas allylic alcohol is reduced to propylene.

Table 1. Allylic Alcohols, Allylic Palladium Complexes, and Allylic Phosphonium Species (with L = PAr_3 = TPPTS)



[a] For the characterization of allylic compounds, see theSupporting Information.

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2. $Pd(TPPTS)_3$ Reactions with Allylic Alcohols: *trans*-2-Buten-1-ol (C_4), Prenol (C_5), Cinnamyl Alcohol (C_9), and Geraniol (C_{10}). The heterolytic cleavage observed with allyl alcohol was extended to other substituted primary allylic alcohols at a regulated pH. In all cases, complex **4** disappeared totally; but with C_5 and C_{10} the reaction was too slow at pH 7 and had to be completed at a more acidic pH. The complex **4** was transformed into a hydrosoluble cationic palladium complex and a hydrosoluble allylic phosphonium species (Table 1). The reactions with C_5, C_9 and C_{10} were very selective. The ^{31}P NMR spectra of the solutions were similar. Each solution showed only one signal near +22 ppm, attributed to TPPTS phosphonium species (**$5a_1$**, **$9a_1$**, **$10a_1$-geranyl**) and two doublets between +25

(39) Larpent, C.; Patin, H *Tetrahedron Lett.* **1988**, *29* (36), 4577–4580.

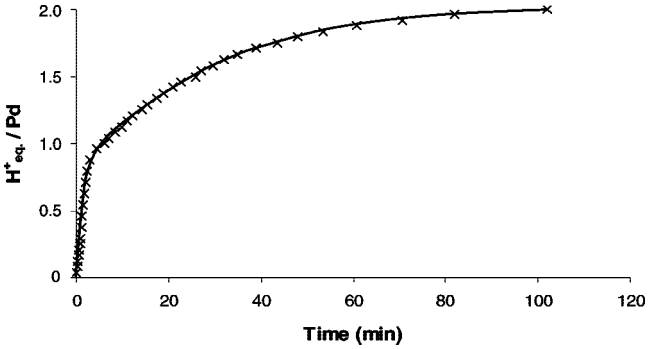


Figure 6. Rate of cinnamyl alcohol reaction with $Pd(TPPTS)_3$: H^+/Pd ratio versus time. Conditions: [Pd] = 0.0055 M in water at 25 °C, cinnamyl alcohol/Pd = 10, initial pH 7, immediately after alcohol addition, pH was maintained at 7 by 0.2 M $HClO_4$ addition.

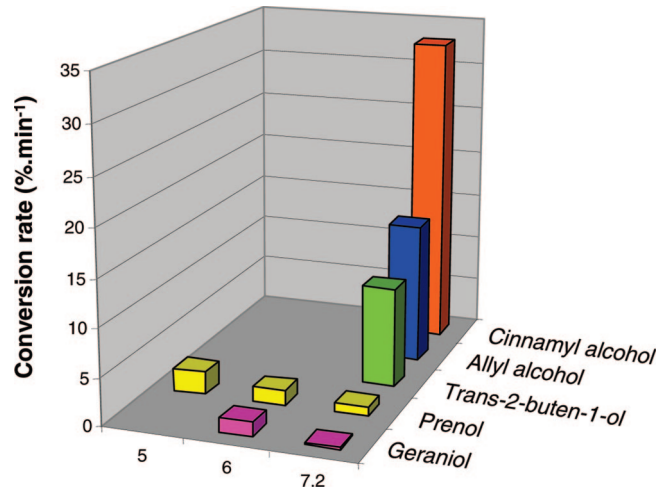


Figure 7. Comparative reactivity of allylic alcohols. Conditions: [Pd] = 0.0055 M in water at 25 °C, initial pH 7, immediately after allylic alcohol addition, pH was maintained at 7 by 0.2 M $HClO_4$ addition. Geraniol and cinnamyl alcohol were not totally soluble in water at the concentration 0.055 M; prenol and geraniol reactions, too slow at pH 7, were completed at a lower pH.

ppm and +30 ppm, attributed to TPPTS palladium (II) complexes $[PdC_5L_2]^+$, $[Pd(syn\text{-}C_9)L_2]^+$, $[Pd(C_{10}\text{-geranyl})L_2]^+$) (Table 1).

In the presence of a large excess of allylic alcohols, it was not possible to characterize the ionic complexes and phosphonium species directly in solution. The strategy was to prepare and characterize the phosphonium salt solutions (^1H NMR, ^{31}P NMR, and mass spectra) and then to characterize the palladium complex solutions in the presence of phosphonium salts, but without an excess of allylic alcohol (Supporting Information).

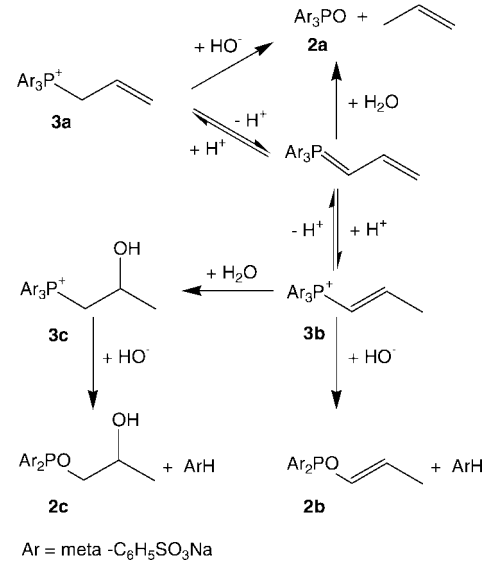
With C_4, complex **4** was transformed into the hydrosoluble cationic palladium complex $[Pd(syn\text{-}C_4)L_2]^+$ (90%),[40] which appeared as a singlet (+27.73 ppm), and into the hydrosoluble phosphonium species **4a$_1$** (95%). In order to characterize the two ions, $[Pd(syn\text{-}C_4)L_2]^+$ was prepared from the reaction of crotylpalladium chloride dimer with 4 TPPTS and **4a$_1$** was prepared directly from the reaction of TPPTS with crotyl chloride.

The reaction of cinnamyl alcohol is given here as an example (Figure 6). Acid addition must be very fast at the beginning of the reaction to keep the pH constant at 7. This behavior was attributed to the preferential formation of the palladium complex. Then, the reaction slowed down. This second step was attributed to the formation of phosphonium salt.

A comparison of the relative reactivities of allylic alcohols during the first step of the reaction (Scheme 2, reaction I) were quantified by the initial rates of acid addition (expressed in (H^+/Pd) min^{-1}), as depicted in Figure 6. It can be concluded that the initial rates of cinnamyl alcohol (0.30 min^{-1}), allyl alcohol (0.20 min^{-1}), and *trans*-2-buten-1-ol (0.10 min^{-1}) were high. More substituted allylic alcohols, such as prenol (0.01 min^{-1}) and geraniol (0.0023 min^{-1}), were less reactive at pH 7. At pH values between 5 and 6, these alcohols were more reactive and led to a complete conversion of **4** at pH 4.5 (Figure 7).

These data indicate that the ionization step in the Tsuji−Trost reaction in water depends on the substitution in position 3 of these primary allylic alcohols. Monosubstitution with the phenyl group has an accelerating effect, while substitution by a methyl has a slightly slowing effect. Disubstituted alcohols such as prenol and geraniol react much more slowly at pH 7, due to presumably a steric hindrance effect. This phenomenon could limit their reactivity in these conditions. In very basic media, the ionization of substituted alcohols could then become the limiting step in catalytic reactions.

Scheme 3. Decomposition of the Allylphosphonium Chloride Salt of TPPTS[47]

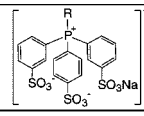
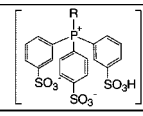
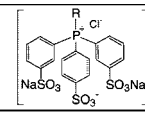
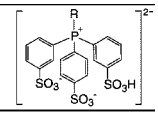


3. Stability of the Allylphosphonium Chloride Salt of TPPTS: Effect of pH and Temperature. It appears from the previous results that the stability of the catalytic system could be related to the stability of the phosphonium cations produced. An irreversible destruction of phosphonium salts should lead to the decomposition of TPPTS by an equilibrium shift (Scheme 2, reaction II), and so, to the precipitation of palladium.

The study of the stability of **3a** versus pH (from 4.75 to 13) and temperature (from 25 to 80 °C) revealed the existence of several transformations (Scheme 3). The transformation into **2a** and propylene consumed OH^- (eq 10). **3a** can also isomerize into the vinylic species **3b**, which can then be hydrated into **3c**. **3b**,**c** are also transformed into the oxides **2b**,**c,** respectively (OH^- consumption results in a variation of pH). In this study, by a judicious choice of pH, temperature, and time conditions,

(40) ^{31}P NMR spectrum: major signal, singlet at 27.73 ppm (90%); other signals, two doublets at 27.03 ppm (10%) (d, J_{PP} = 40 Hz) and 25.45 ppm (d, J_{PP} = 40 Hz), probably the anti isomer $[Pd(anti\text{-}C_4)L_2]^+$, which should have signals similar to the signals of the complexes $[Pd(C_5)L_2]^+$, $[Pd(C_9)L_2]^+$, and $[Pd(C_{10})L_2]^+$. In the case of the preparation of $[Pd(syn\text{-}C_4)L_2]^+$ from the reaction of crotylpalladium chloride dimer with four TPPTS, the same spectrum was obtained.

Table 2. Selected Negative-Ion Electrospray Mass Spectrum Data of 3a–c[a]

R				
 **3a**	563.1 (563.0)	541.1 (541.0)	620.9 (620.9)	270.2 (270.0)
 **3b**	563.1 (563.0)	541.1 (541.0)	620.8 (620.9)	270.1 (270.0)
 **3c**	580.9 (581.0)	558.9 (559.0)	638.8 (638.9)	279.0 (279.0)

[a] The *m*/*z* required is given in parentheses.

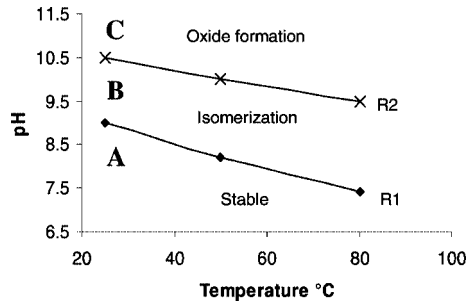


Figure 8. Stability of the allylphosphonium salt of TPPTS **3a**. R1 corresponds to a 1% decomposition rate of **3a** into **3b**,**c** (80 °C pH 7.5; 50 °C pH 8.5; 25 °C pH 9). R2 corresponds to a 1% decomposition rate of **3a** into oxides (80 °C pH 9.5; 50 °C pH 10; 25 °C pH 10.6).

we were able to concentrate aqueous solutions of **3b**,**c** and **2b**,**c** products for their characterization in solution by ^{31}P, ^{13}C, and ^{1}H NMR. The ionic nature of species **3a**−**c** was demonstrated by mass spectroscopy (Table 2 and the Supporting Information).

In a highly basic medium (pH above 11), the main decomposition product is TPPTS oxide **2a** (with **2b**,**c** if conditions are less basic). At lower pH values (between 7 and 10), **3b**,**c** appear, whereas the decomposition into oxide **2a** is much slower (<1% h^{-1}). In neutral or slightly acidic medium, there is still a very low decomposition of **3a** at 80 °C (0.32% h^{-1} at pH 7 and 0.03% h^{-1} at pH 4.7).

These transformation reactions of phosphonium salt **3a** can be quantified in a simplified way by considering the curves that allow a 1% h^{-1} decomposition of **3a** (Figure 8). The curve R1 shows the decomposition of **3a** into **3b**,**c** also at 1% h^{-1}, and the curve R2 shows the transformation of **3a** into oxides at 1% h^{-1}. In the area A located below R1, **3a** can be considered stable if the pH is below 9 at room temperature and below 7.5 at 80 °C. In the area C located above R2, **3a** decomposed quickly into oxides if the pH is above 10.6 at room temperature and above 9.5 at 80 °C. In the area B located between R1 and R2 with a gap of 1.5 pH units, the decomposition into **2a** is very slow, but **3a** is quickly converted into **3b**,**c** on heating (see the Supporting Information).

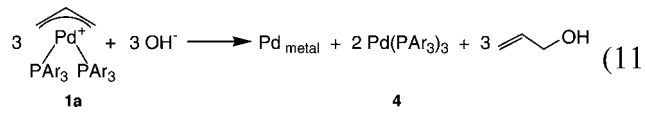
4. Stability of [Pd(η^3-allyl)(TPPTS)$_2$]$^+$. An aqueous solution of **1a** was prepared by the reaction of allylpalladium chloride dimer with TPPTS (solution **S1** of **1a** at 0.0825 M) in the presence of chloride at the same concentration and oxide **2a** (3−5 mol %/Pd, pH around 7).

a. Stability at Room Temperature. The solution **S1** was stable for several months at room temperature under argon. No reaction occurred in acidic medium according to NMR analysis (^{31}P NMR spectra remained unchanged), while a decomposition was observed in basic medium.

At room temperature upon the gradual addition of 1 M sodium hydroxide to a dilute solution of **1a**, there was no decomposition up to around pH 12. However, at pH 12.5, a blackening of the solution occurred, and then metallic palladium precipitated. The ^{31}P NMR analysis of the solution after decomposition showed the disappearance of the signal of **1a** at +25.60 ppm, the appearance of the complex **4** Pd(TPPTS)$_3$, corresponding to 50% of palladium, and **2a** (with the surface ratio **2a**/**4** = 0.36). We point out here that complex **1a**, prepared by the reaction of allyl alcohol in excess with Pd(TPPTS)$_3$ without acidification, was stable for several weeks at room temperature at pH 11.65.

At pH 13.87 (0.75 M NaOH solution) the reaction proceeded instantaneously: a metallic palladium precipitate appeared and **1a** was also transformed into **4** (48 mol %/Pd) and **2a** (12 mol %/Pd). The evolution of propylene (12 mol %/Pd) is in agreement with a partial oxidation of TPPTS in **1a** into **2a**. However, two unidentified phosphorus products also appeared (broad signals at +27 and +30 ppm), showing that decomposition proceeds via another mechanism.

A possible reaction for the formation of the metallic palladium is depicted in eq 11. Allylic alcohol is not observed in the reaction medium, as it would be transformed immediately into propanal upon an aldolization reaction.



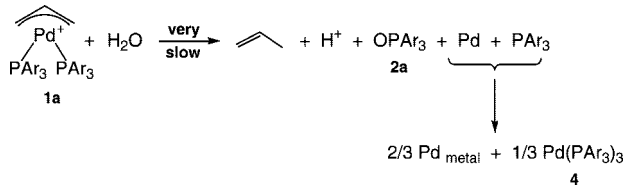
1a **4** (11)

In conclusion, complex **1a** is stable at room temperature in aqueous medium over a fairly wide range of pH values, but not beyond pH 12. Above this pH, a dark color appears followed by the precipitation of palladium.

b. Stability at 80 °C. At 80 °C, complex **1a** decomposes slightly at pH 7.60. After 12 h, the pH has decreased from 7.60 to 3.97 (H^+ released 1%/Pd) and propylene has evolved (2.5%) with OTPPTS formation (1.5%) and an unidentified phosphorus compound X at +27.80 ppm (1%). The precipitation of metallic palladium was not observed in the Schlenk tube, but it should correspond to a palladium concentration decrease of only 20 ppm. Other tests at 80 °C under similar conditions confirmed the intrinsic instability with a pH decrease and sometimes the appearance of a small amount of metallic palladium.

At this pH, the propylene released cannot be explained by phosphonium salt **3a** decomposition, since **3a** is stable under the reaction conditions. Another hypothesis is a direct reaction of the complex with water involving propylene and **2a** formation

Scheme 4



and an acidity increase (Scheme 4). One part of palladium precipitates, the other part remains as complex **4** or unidentified dimers.

c. Stability at 80 °C in the Presence of 3a. A solution obtained from the reaction of **4** with a small excess of allyl alcohol at pH 7.4 according to eq 5 ([**1a**] = [**3a**] = 0.011 M, $[\text{allyl alcohol}]_{\text{remaining}} = 0.003$ M) was heated at 80 °C for 14 h. After the reaction, the pH did not change and no propylene was observed in the gaseous phase. The concentrations of **1a** and **2a** remained the same, but **3a** was transformed (21%) into phosphonium salt **3b**. This conversion of about 1.5% h^{-1} is in agreement with the intrinsic stability of **3a** previously observed (estimated at 1% h^{-1} at pH 7.5) (Figure 8).

The better stability of complex **1a** in the presence of **3a** was confirmed by two comparison tests without allyl alcohol. The addition of **3a** reduced both the pH variation and propylene release without palladium precipitation at 80 °C (Figure 9).

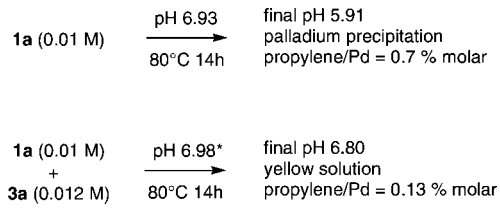


Figure 9. Beneficial effect of **3a** on **1a** stability. In the second reaction, **3a** isomerization into **3b** was observed (1.6%/14 h: i.e., 0.11% h^{-1}). Without palladium, the **3a** isomerization rate in a pH range 6.5−7.0 was estimated at 0.1% and 0.38% h^{-1} (see the Supporting Information).

Another solution obtained from the reaction, according to eq 5 at pH 9 (**1a** = **3a** = 0.01 M, $[\text{allyl alcohol}]_{\text{remaining}} = 0.045$ M), was heated for 17 h, at 80 °C under the same conditions. After heating, the pH was 8.3 (0.03 equiv of H^+/Pd), propylene was evolved (0.027 equiv/Pd), and a slight darkening of the solution was observed, meaning that a very small amount of metallic palladium appeared in suspension and precipitated after cooling. These results show that decomposition of the complex **1a** in the presence of **3a** occurs more rapidly at pH 9 than at pH 7. The ^{31}P NMR spectrum of the solution shows that **3a** isomerizes into **3b** (**3b/3a** = 98/2) after heating. We can propose that the disappearance of the beneficial effect of **3a** at higher pH is due to its rapid thermal isomerization into **3b**.

These results are in agreement with palladium precipitation observed in basic medium during phenol allylation[24] and butadiene hydromerization.[7a]

Conclusion

We demonstrated that the reaction between $Pd(TPPTS)_3$ and allylic alcohols led to the formation of two cationic compounds: a palladium complex and an allylic phosphonium salt. The π-allyl cationic palladium complex is stable over a wide range of pH values at room temperature but is highly unstable upon heating. A detailed investigation of degradation reactions of the allylphosphonium salt of TPPTS showed the harmful effect of basic media and temperature on its stability. Therefore, the disappearance of the excess of TPPTS through phosphonium salt formation and degradation reduces the stability of the cationic palladium complex. The metallic palladium precipitation in the Tsuji−Trost reaction or diene telomerization has probably several causes. However, this study showed that, over a narrow range of pH and temperature, the phosphonium salt of TPPTS and the π-allyl cationic palladium complex were stable.

A second important point is the synthesis of new hydrosoluble cationic allylic palladium complexes from *trans*-2-buten-1-ol, prenol, and geraniol that are stable in water at room temperature. Formally, these complexes could also result from the reaction of corresponding dienes with $Pd(TPPTS)_3$ and a proton from the aqueous solution. A knowledge of the formation conditions and reactivity of these palladium(II) complexes toward nucleophiles or water could afford a better understanding of the catalyzed functionalization or hydration of butadiene into butenyl or octadienyl compounds. These complexes and their isomers could also govern the selectivity of the functionalization reactions of dissymmetric dienes, such as isoprene or myrcene, and of the isomerization reaction of butenols as well as that of Tsuji−Trost reactions in water.

Experimental Section

1. Chemical Reagents. All the following reagents were used as supplied by the manufacturer: $Pd(OAc)_2$, allylpalladium chloride dimer, crotylpalladium chloride dimer, allyl alcohol, crotyl chloride, *trans*-2-buten-1-ol, cinnamyl alcohol, 3-methyl-2-buten-1-ol (prenol), geraniol (Aldrich); $HClO_4$, H_2SO_4, NaOH, CH_3COONa, CH_3COOH (Laurylab); D_2O (SDS). pH buffers 4.01, 7.01, and 10.01 at 25 °C were supplied by Bioblock (France). TPPTS and TPPDS were gifts from Ruhrchemie-Celanese (TPPTS with TPPDS 5%, TPPTS oxide 3−5.2%; TPPDS with TPPDS oxide 1%). TPPMS (with TPPMS oxide 1%) was prepared according to the method of Chatt et al.[41] The trisodium salt of allyltris(*m*-sulfophenyl)phosphonium chloride **3a** (with TPPTS oxide 5.2%, disodium salt of allylbis(*m*-sulfophenyl)phenylphosphonium chloride 5%, trisodium salt of propenyltris(*m*-sulfophenyl)phosphonium chloride **3b** 0.6%) was prepared according to our previous report.[24] Water was distilled and degassed with argon.

2. Measurements. ^{31}P NMR, ^{1}H NMR, and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer (external reference for phosphorus analyses H_3PO_4 85%). The samples of palladium TPPTS complexes or phosphorus compounds were dissolved in 0.5 mL of D_2O or 0.4 mL of water with 0.1 mL of D_2O.

Mass spectra were recorded on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive ions (+) or negative ions (−) in the ESI mode. Samples (in methanol/dichloromethane/water, 45/40/15 v/v/v containing 0.1% of formic acid) were infused directly into the source (5 μL min^{-1}) using a syringe pump. The following source parameters were applied: spray voltage 3.0−3.5 kV, nitrogen sheath gas flow 5−20 arbitrary units. The heated capillary was held at 200 °C.

The pH measurements were performed with a PHN 330 T pH meter and a combined electrode (Tacussel, France).

All experiments were performed under an inert atmosphere using argon and using GAN syringes with 100 mm needles (Bioblock, France). The oxygen concentration in water was measured with a Bioblock Scientific 9071 oxymeter and found to be less than 0.1 ppm.

The propylene concentration in the gas phase was determined by GC analysis using an HP-5890 instrument with an HP-5 capillary

(41) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 264–276.

column (30 m × 0.25 mm) and an HP GCD series mass spectrometer.

3. Pd(TPPTS)$_3$ Water Solution Preparation. Pd(TPPTS)$_3$ solution (**4**) was prepared from Pd(OAc)$_2$ + *n*TPPTS ($4 < n < 4.5$) by a redox process: the excess of TPPTS reduced palladium(II) to palladium(0). The pH was controlled by NaOH additions.[27a] At the end of the reaction, the pH was brought to 7.0−7.2. Conditions: [Pd] = 0.06−0.10 M, OTPPTS/Pd molar ratio 1.2, TPPTS/Pd = 3−3.5, sodium acetate/Pd = 2 (using D_2O and NaOH/D_2O, a D_2O Pd(TPPTS)$_3$ solution was prepared, [Pd] = 0.053 M).

4. Typical Allylic Compound Reaction with Pd(TPPTS)$_3$ at Room Temperature. A 20 mL Schlenk tube was equipped with a pH electrode. Distilled water and aqueous Pd(TPPTS)$_3$ solution were added,[42] and the pH adjusted to 7[43] with 0.2 M NaOH or 0.2 M $HClO_4$ (volume of the solution 5 mL, [Pd] = 0.0055 M). The allylic compound was then added with a syringe (except cinnamyl alcohol, which is solid). The solution was homogeneous, except for cinnamyl alcohol and geraniol, which are not soluble enough at 0.055 M. Within a few seconds, the pH increased. The 0.2 M $HClO_4$ was added with GAN syringes to keep the pH at 7[44,45] with variations between 6.8 and 7.2. After 100 min, the pH became stable. A 0.026 mL portion of $HClO_4$ (2 equiv/Pd) was poured in (solution **S1** with allyl alcohol).

The ^{31}P NMR spectrum of solution **S1** (0.4 mL) + D_2O (0.1 mL) exhibited two new signals: 25.61 ppm (**1a**)[46] and 22.31 ppm (**3a**). The Pd(TPPTS)$_3$ signal at 23.85 ppm fully disappeared, and the amount of OTPPTS **2a** remained unchanged. The ratio of the intensity of the signals was close to 1.20/2.00/1.00 (**2a/1a/3a**).

5. Reaction of the Allylphosphonium Chloride Salt of TPPTS with Pd(TPPTS)$_3$ at Room Temperature. In a 10 mL Schlenk tube equipped with a magnetic stirrer, 0.1 mmol of **3a** was dissolved in 1.5 mL of water and 0.5 mL of D_2O. A 0.5 mL portion of Pd(TPPTS)$_3$ aqueous solution (0.059 M) was added. The ^{31}P NMR spectra of the aqueous solution remain unchanged after 20 min or 1 day or after heating for 3 h at 55 °C (equilibrium among **3a**, **4**, **1a**, and TPPTS).

6. Stability of [Pd(η^3-allyl)(TPPTS)$_2$]$^+$(1a). a. Slow Decomposition. A 0.1 mL portion of 1 M NaOH was added to 5.5 mL of a 0.0071 M **1a** solution (pH 7.5) in 60 min to reach pH 12.2 and then 0.2 mL to reach pH 12.5. A blackening of the solution occurred; palladium precipitated (see section 4a).

b. At pH 13.87 (0.75 M NaOH Solution). A 0.5 mL portion of a 0.0825 M **1a** solution in D_2O was added to 1.5 mL of 1 M NaOH in D_2O. Palladium precipitated immediately. The gaseous phase contained 12 mol % of propylene/**1a** (see section 4a).

c. At 80 °C. Portions of the solutions amounting to *x* mL were poured in a Schlenk tube. After *y* hours at 80 °C and cooling to room temperature, propylene was analyzed in the gaseous phase, the pH was measured, and water was analyzed: (i) $x = 2$ mL (**1a** 0.016 M, pH 7.6), $y = 14$ h (final pH 3.97) (see section 4b); (ii) $x = 5$ mL (**1a** 0.01 M + **3a** 0.012 M from the reaction of **4** with allyl alcohol in low excess [allyl alcohol] = 0.003 M, pH 7.4), $y = 12$ h (final pH 7.40) (see section 4c); (iii) $x = 5$ mL (**1a** 0.01 M, pH 6.93), $y = 14$ h (final pH 5.91) (see section 4c); (iv) $x = 5$ mL (**1a** 0.01 M + **3a** 0.01 M, pH 6.98), $y = 14$ h (final pH 6.80) (see section 4c); (v) $x = 5$ mL (**1a** 0.01 M + **3a** 0.01 M from the reaction of **4** with allyl alcohol in excess [allyl alcohol] = 0.045 M, pH 9.0), $y = 17$ h (final pH 8.3) (see section 4c).

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Supporting Information Available: Text and figures giving experimental procedures and spectral and analytical data for the products of the reaction of Pd(TPPTS)$_3$ with *trans*-2-buten-1-ol, prenol, cinnamyl alcohol, geraniol and allyl alcohol as limiting reagent and for products obtained from the allylphosphonium salt of TPPTS decomposition and data for the estimation of the allylphosphonium salt of TPPTS decomposition rate and preparation details and characterization data for homologous complexes with TPPTS (**1a**), TPPDS (**1b**), and TPPMS (**1c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) With an excess of TPPTS (4 equiv of TPPTS/Pd), 6 equiv of $HClO_4$/Pd was added. Five equivalents of TPPTS/Pd was transformed into **3a**.

(43) Or at pH 3 and 9 with allyl alcohol (pH influence study).

(44) Geraniol and prenol reactions were slow at pH 7. The reactions were faster at pH 6 and 5. Total conversions were obtained at pH 4.5.

(45) With allyl alcohol ($R = 10$) without acid addition, the pH was increased and measured over 5.5 h. ^{31}P NMR spectrum after 2 h: **1a/4**, 15%; **3a/4**, 4%. After 1 day, the pH of the solution was 11.65 and propylene was identified in the gas phase. The conversion of **4** was 100% into **1a**. **3a** had disappeared, but the amount of TPPTS oxide **2a** present in the solution had increased (**2a/1a** = 2.20/1).

(46) Since TPPTS contained 5% of TPPDS, a small concentration of [Pd(allyl)(TPPTS)(TPPDS)]$^+$ was present: ^{31}P NMR peaks at 25.98, 25.61 ppm (major) and 25.22, 24.97 ppm. By addition of TPPDS to the allylation reaction of **4** by allyl alcohol (TPPDS/TPPTS = 1.6/3), an increase of signals due to TPPDS was actually observed. These peaks were also observed after the reaction of allylpalladium dimer and TPPTS. .

(47) Homologous compounds with triphenylphosphine, **3a′**−**c′** and **2b′**,**c′**, were already synthesized with available ^{1}H NMR analysis (except **2c′**). **3a′**, allyltriphenylphosphonium chloride, was synthesized from the TPP reaction with allyl chloride,[47a] **3b′**, 2-propenyltriphenylphosphonium bromide, from **3a′** bromide (prepared from TPP and allyl bromide) isomerization in a refluxing 2-methoxyethanol solution,[47b] **3c′**, 2-hydoxypropyltriphenylphosphonium hydroxide, from TPP reaction with propylene oxide,[47c] **3c′** iodide, from TPP reaction with propylene oxide, NaI, and carbon dioxide,[47d] (d); **2b′**, propenyldiphenylphosphine oxide, from $(C_6H_5)_2POCl$ and 1-bromopropene Grignard reagent,[47e] and **2c′**, 2-hydoxypropyldiphenylphosphine oxide, from $(C_6H_5)_2HPO$ reaction with propylene carbonate:[47f] (a) Buchi, G.; Wüest, H, *Helv. Chim. Acta* **1971**, *188*−*189*, 1681–1687. (b) Falvello, L. R.; Fernandez, S.; Larraz, C.; Llusar, R.; Navarro, R.; Urriolabeitta, E. P. *Organometallics* **2001**, *20*, 1424–1436. (c) Christol, H.; Christau, H.; Soleiman, M. *Tetrahedron Lett.* **1976**, *37*, 3321–3324. (d) Huang, J.; Sin, M. *J. Org. Chem.* **2003**, *68* (17), 6705–6709. (e) Ducan, M.; Gallagher, M. J. *Org. Magn. Reson.* **1981**, *15* (1), 37–42. (f) Tarpey, P, K.; Martin, G. *J. Org. Chem.* **1962**, *27*, 1817–1823.