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Allylic Substitution Mediated by Water and Palladium: Unusual Role of a Palladium(II) Catalyst and ESI-MS Analysis

Carole Chevrin, Jean Le Bras, Françoise Hénin, and Jacques Muzart*

Unité Mixte de Recherche "Réactions Sélectives et Applications", CNRS-Université de Reims Champagne-Ardenne, BP 1039, 51687 Reims Cedex 2, France

Anna Pla-Quintana and Anna Roglans*

Department of Chemistry, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain

Roser Pleixats

Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain

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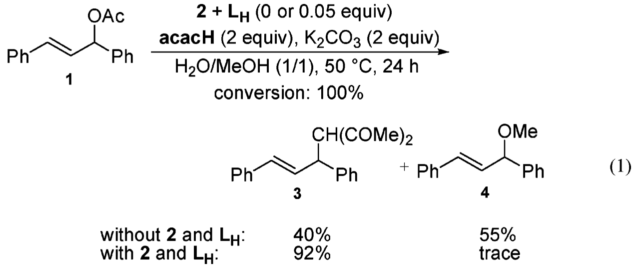
Summary: Allylic substitution of PhCH(OAc)CH═CHPh by $CH_2(COMe)_2$ in a basic MeOH/H_2O mixture could be achieved in the absence of a palladium catalyst and lead to a mixture of PhCH(CH$(COMe)_2$)CH═CHPh and PhCH(OMe)CH═CHPh in 40% and 55% yields, respectively. The process is induced by water, and nucleophilic attack addition occurred on a stabilized carbocation as the intermediate. Addition of a catalytic amount of $PdCl_2(CH_3CN)_2$ did not accelerate the reaction but improved the selectivity, and PhCH(CH$(COMe)_2$)CH═CHPh was then obtained in 92% yield while PhCH(OMe)CH═CHPh was observed in trace amounts. An ESI-MS analysis of the reaction mixture led us to assume that a palladium acetylacetonate complex is involved in the formation of PhCH(CH$(COMe)_2$)CH═CHPh.

The use of water as solvent for organic synthesis is very attractive for environmental, economic, and safety reasons,[1] and we have recently shown that water may promote the allylic substitution of 1-acetoxy-1,3-diphenylpropene (**1**) with high yields in the absence of any palladium complex.[2] However, with acetylacetone (**acacH**) as nucleophilic species in a MeOH/H_2O mixture, the selectivity toward the C−C bond formation was low; this was improved by addition of catalytic amounts of a Pd^{II} salt, namely $PdCl_2(CH_3CN)_2$ (**2**) and the hydrophilic ligand $[(HOCH_2CH_2NHCOCH_2)_2NCH_2]_2$ (**L_H**).[3] The reaction times needed to achieve the complete consumption of **1** were similar under both conditions (eq 1).[2]



Electrospray ionization mass spectrometry (ESI-MS)[4] allows the observation of intermediates involved in catalytic reactions, the data being directly acquired from the reaction mixture.[5] ESI-MS has been recently used for the screening of palladium catalysts[6] and for the determination of the mechanism of the Heck reaction with arene diazonium salts.[7] Therefore, we have used this method to investigate the role of **2** and **L_H** in the reaction of **1** with **acacH** under aqueous conditions. The identification of the species detected by ESI-MS was aided by comparison between the observed and calculated isotope distribution patterns. Because ^{46}Pd and ^{17}Cl display six and two isotopes, respectively, the ions containing these atoms should be mass-detected as clusters of isotopomeric ions whose center depends on the most abundant isotope (106 for Pd and 35 for Cl).[8] All ESI-MS analyses were performed with samples dissolved in 1/1 MeOH/H_2O, since this mixture is the most appropriate in the allylic alkylation of **1** in the presence of **2** and **L_H**.[2] The mobile phase used in all ESI experiments was a 70:30 mixture of MeOH and H_2O.

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* To whom correspondence should be addressed. E-mail: jacques.muzart@univ-reims.fr (J.M.); anna.roglans@udg.es (A.R.).

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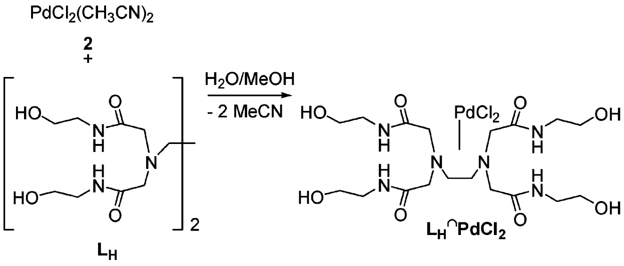
10.1021/om0495877 CCC: $27.50

Table 1. Electrospray Mass Spectral Data for Various Mixtures

entry	mixture	identified species[a]
1	**1**, room temp	ESI(+): 193, $[\mathbf{1} - OCOCH_3]^+$
2	$\mathbf{L_H}$, room temp	ESI(+): 465, $[\mathbf{L_H} + H]^+$; 487, $[\mathbf{L_H} + Na]^+$
3	$\mathbf{L_H} + PdCl_2(CH_3CN)_2$, room temp	ESI(+): 465, $[\mathbf{L_H} + H]^+$; 567−574 (569), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$; 603−611 (607): $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl]^+$ ESI(−): 601−609 (605), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - 2H]^-$; 637−645 (641), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - H]^-$
4	$\mathbf{1} + \mathbf{L_H} + PdCl_2(CH_3CN)_2$, room temp	ESI(+): 193, $[\mathbf{1} - OCOCH_3]^+$; 465, $[\mathbf{L_H} + H]^+$; 567−574 (569), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$; 603−611 (607), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl]^+$
5	$\mathbf{1} + \mathbf{L_H} + PdCl_2(CH_3CN)_2 + 2$ **acacH** + 2 K_2CO_3, 50 °C for 1 or 24 h	ESI(+): 331, $[\mathbf{3} + K]^+$; 503, $[\mathbf{L_H} + K]^+$; 605−612 (607), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + K]^+$; 641−649 (645), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - H + K]^+$; 705−712 (707), $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - H - X + K]^+$ (X = Cl, OAc)
6	$\mathbf{1} + \mathbf{L_H} + PdCl_2(CH_3CN)_2 + 2$ **acacH** 2 K_2CO_3, 50 °C for 24 h	ESI(−): 565−572 (567), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 3H]^-$; 601−609 (605), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - 2H]^-$; 701−709 (705), $[\mathbf{L_H}{}^\frown\mathbf{PdCl}{}^\frown\mathbf{acac}$ - $H]^-$
7[b]	$\mathbf{L_H} + PdCl_2(CH_3CN)_2 +$ **acacH** 2 K_2CO_3, room temp	ESI(+): 567−574 (569), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$; 605−612 (607), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + K]^+$; 641−649 (645), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - H + K]^+$; 667−674 (669), $[\mathbf{L_H}{}^\frown\mathbf{PdCl}{}^\frown\mathbf{acac}$ - $Cl]^+$; 705−712 (707), $[\mathbf{L_H}{}^\frown\mathbf{PdCl}{}^\frown\mathbf{acac} - H - Cl + K]^+$
8	$\mathbf{L_H} + PdCl_2(CH_3CN)_2 +$ **acacH**, room temp	ESI(+): 567−574 (569), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$; 603−611 (607), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl]^+$; 667−674 (669), $[\mathbf{L_H}{}^\frown\mathbf{PdCl}{}^\frown\mathbf{acac} - Cl]^+$
9[b]	**1** (excess) $+ \mathbf{L_H} + PdCl_2(CH_3CN)_2 +$ **acacH** + 2 K_2CO_3, 50 °C for 1.5 h	ESI(+): 293, $[\mathbf{3} + H]^+$; 331, $[\mathbf{3} + K]^+$; 567−574 (569), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$; 605−612 (607), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + K]^+$; 641−649 (645), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - H + K]^+$; 667−674 (669), $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - X]^+$ (X = Cl, OAc); 705−712 (707), $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - H - X + K]^+$ (X = Cl, OAc)
10	$\mathbf{1} + 0.2\ \mathbf{L_H} + 0.2\ PdCl_2(CH_3CN)_2 +$ 2 **acacH** + 2 Na_2CO_3, 50 °C for 1.5 h	ESI(+): 315, $[\mathbf{3} + Na]^+$; 487, $[\mathbf{L_H} + Na]^+$; 589−596 (591), $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + Na]^+$; 689−696 (691), $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - H - X + Na]^+$ (X = Cl, OAc)
11	$\mathbf{1} + Pd(PPh_3)_4$	ESI(+): 559−566 (561), $[Pd(Ph(CH)_3Ph)(PPh_3)]^+$; 821−828 (823), $[Pd(Ph(CH)_3Ph)(PPh_3)_2]^+$

[a] Reported *m*/*z* values are from the lowest to the highest mass in the isotope envelope of the clusters; the value in parentheses is the most abundant peak. [b] An analogous experiment was performed using Na_2CO_3 instead of K_2CO_3, observing the same species as sodium adducts. The observation of the same species as sodium and potassium adducts confirms the identity of the species detected.

The ESI(+)-MS of **1** showed one peak at *m*/*z* 193 corresponding to the cationic allylic structure $[\mathbf{1} - OCOCH_3]^+$ (Table 1, entry 1) while the spectrum of $\mathbf{L_H}$ afforded two peaks at *m*/*z* 465 and 487, consistent with the protonated ligand $[\mathbf{L_H} + H]^+$ and the sodium adduct $[\mathbf{L_H} + Na]^+$ (entry 2).[9] The analysis of the ESI(+) mass spectrum of a 1/1 mixture of **2** and $\mathbf{L_H}$ led us to assume the formation of the complex $\mathbf{L_H}{}^\frown\mathbf{PdCl_2}$ (eq 2),



(2)

since two clusters attributable to the cationic species $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - H]^+$ and $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl]^+$ were observed at *m*/*z* 569 and 607, respectively (entry 3). Injecting the same mixture in negative-ion mode ESI(−) showed a cluster centered at *m*/*z* 605, corresponding to the same species as above, but as the anionic form $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - 2H]^-$. In addition, a new cluster was observed centered at *m*/*z* 641 and was consistent with the species $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - H]^-$ (entry 3).

The ESI(+)-MS spectrum of a stoichiometric mixture of **1**, **2**, and $\mathbf{L_H}$ (entry 4) afforded the signals of the clusters already observed in entries 1−3, and furthermore, a similar spectrum was obtained after heating the mixture at 50 °C for 1.5 h. No new species were observed on working in negative-ion mode ESI(−).

The reaction of an equimolecular mixture of **1**, **2**, and $\mathbf{L_H}$ with 2 equiv of both **acacH** and K_2CO_3 in MeOH/H_2O at 50 °C was then monitored (entry 5). After 1 h, the ESI(+) mass spectrum showed a variety of signals: (i) two peaks at *m*/*z* 331 and 503, corresponding to the potassium adducts of the substitution product $[\mathbf{3} + K]^+$ and the ligand $[\mathbf{L_H} + K]^+$ respectively;[10] (ii) two clusters at *m*/*z* 607 and 645, attributed to the cationic species $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + K]^+$ and $[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - Cl - H + K]^+$; one cluster at *m*/*z* 707, attributed to $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - H - X + K]^+$ (X = Cl, OAc), consistent with the formation of the palladium enolate complex $\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac}$.

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(8) Electrospray mass spectrometry analyses were recorded on a Navigator quadrupole mass spectrometer (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. The instrument was operated either in the positive ESI(+) or in the negative ESI(−) ion mode at a probe tip voltage of 3 kV. The samples were taken directly from the reaction mixture and dissolved in MeOH to get an approximate concentration of 4 mM. The samples were introduced into the mass spectrometer ion source directly through a Rheodyne injector with a 20 μL sample loop. The mobile phase flow (100 μL/min of 70/30 v/v MeOH/H_2O) was delivered by a P2000 HPLC pump (ThermoQuest) to the vaporization nozzle of the electrospray ion source (165 °C for ESI(+) and 140 °C for ESI(−)), and nitrogen was employed as both a drying and a nebulizing gas. Skimmer cone voltages were varied between 10 and 100 eV. Spectra were typically an average of 15−20 scans. Theoretical isotope patterns were calculated by use of the Isoform program and used to aid assignment.

(9) Association of the substrate with ions is common. $[M + H]^+$ and $[M + Na]^+$ are often observed; the latter appears from the reaction with traces of cations present even in HPLC-grade solvent.[4c]

(10) No adduct was observed between product **3** and Pd(II) in the reaction medium or in a mixture of **3**, $\mathbf{L_H}$, and **2**.

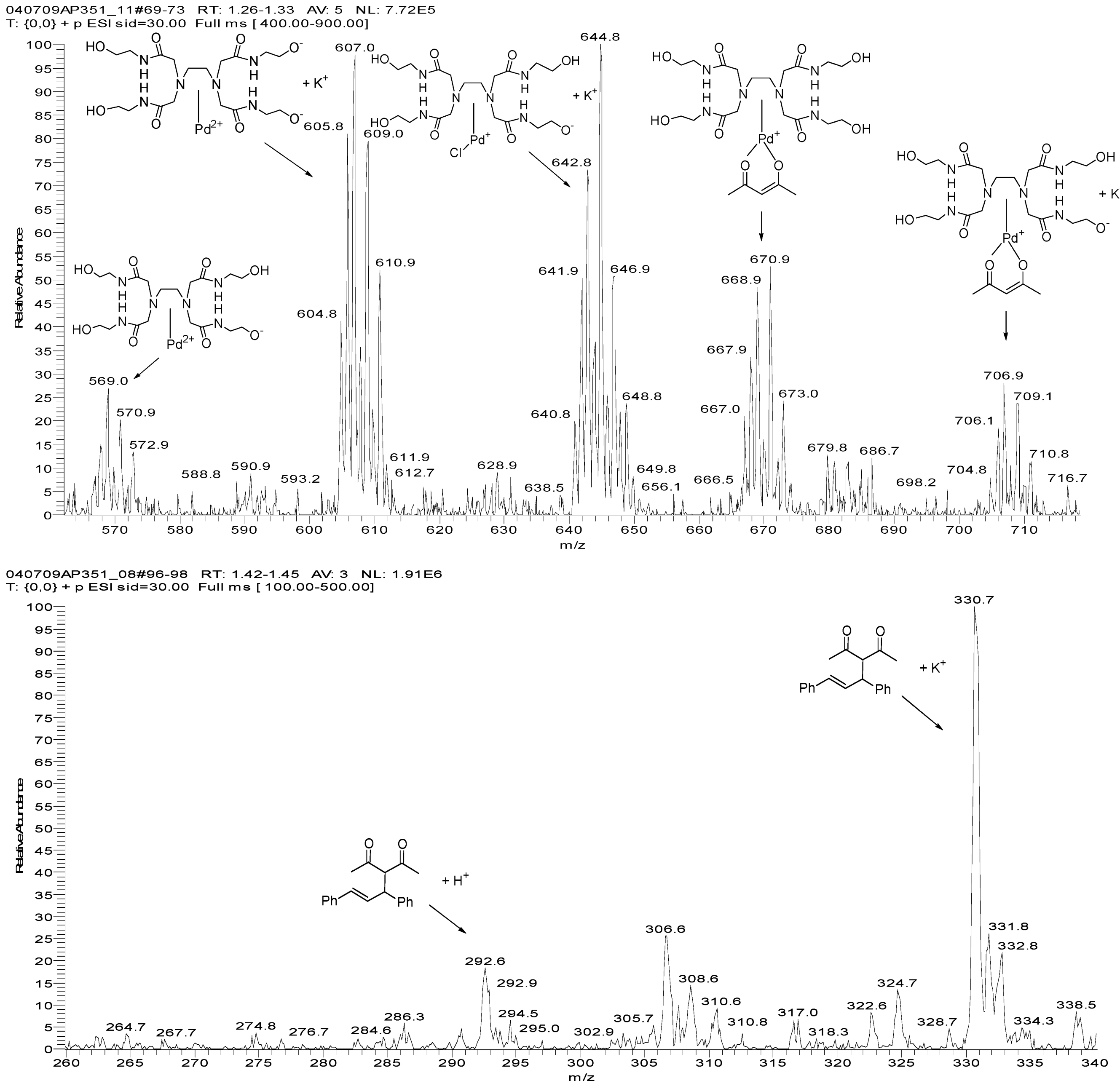
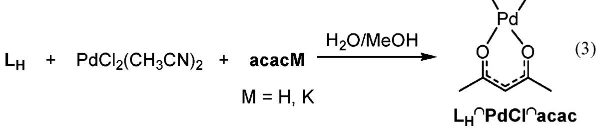


Figure 1. ESI(+)-MS spectrum of the reaction mixture: **1** (excess) + $\mathbf{L_H}$ + $PdCl_2(CH_3CN)_2$ + **acacH** + 2 K_2CO_3 at 50 °C after 1.5 h of reaction (entry 9 in Table 1).

Prolonging the reaction time to 24 h or working with catalytic amounts of **2** and $\mathbf{L_H}$ (0.2 equiv of each) afforded similar data. However, in negative-ion mode ESI(−) a new cluster was observed centered at *m*/*z* 705 corresponding to [$\mathbf{L_H}$⌒**PdCl**⌒**acac** - H]$^-$ (entry 6). Although the anion [$\mathbf{L_H}$⌒**PdOAc**⌒**acac** − H]$^-$ has not been detected by ESI(−), such a species where Cl has been substituted by OAc cannot be excluded. Thus, an intermediate of general formula $\mathbf{L_H}$⌒**Pd**⌒**Xacac** is considered (X = Cl, OAc).

It should be noted that the enolate complex $\mathbf{L_H}$⌒**PdCl**⌒**acac** was detected at room temperature from $\mathbf{L_H}$ + **2** + **acacH** in the presence of K_2CO_3 (entry 7) and even in the absence of a base (entry 8). Its formation may therefore be explained by direct reaction of **2** with **acacH** or by a transmetalation reaction with the potassium enolate **acacK** (eq 3).[11,12]



(3)

The addition of an excess of **1** to the sample examined in entry 7 followed by heating at 50 °C for 1.5 h led to an ESI(+) mass spectrum showing the above signals (as K^+ adducts) and also those of **3** (entry 9 and Figure 1). Under catalytic conditions, the use of Na_2CO_3 as base instead of K_2CO_3 afforded two peaks at *m*/*z* 315 and 487 corresponding to [**3** + Na]$^+$ and [$\mathbf{L_H}$ + Na]$^+$ and two clusters at *m*/*z* 591 and 691 consistent with the cations

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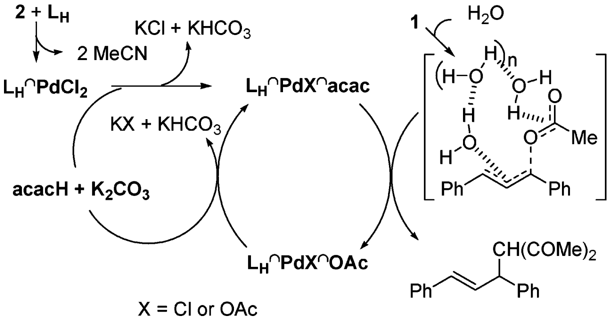
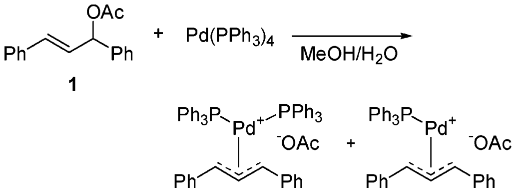
[11] Several kinds of coordination modes are known between Pd(II) and acetylacetone; see: (a) Kanda, Z.; Nakamura, Y.; Kawaguchi, S. *Inorg. Chem.* **1978**, *17*, 910. (b) Otani, Y.; Nakamura, Y.; Kawaguchi, S.; Okeya, S. Hinomoto, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1467. The O,C,O′ chelation was chosen in our case according to the reactivity of the palladium enolate complex with **1**.

Scheme 1



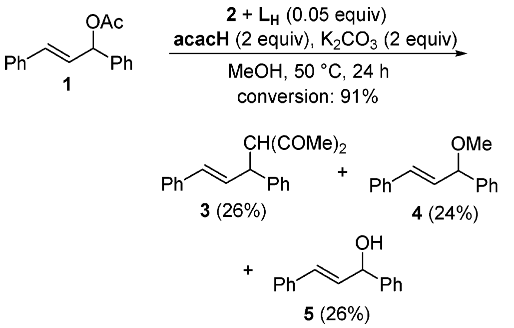
$[\mathbf{L_H}{}^\frown\mathbf{PdCl_2} - 2Cl - 2H + Na]^+$ and $[\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac} - H - X + Na]^+$ (X = Cl, OAc) (entry 10).

Under all above experimental conditions, we have not been able to detect a cluster containing a $Ph(CH)_3Ph$ fragment, although (η^3-allyl)palladium intermediates are observable by ESI(+)-MS under Pd^0 conditions. Indeed, two clusters centered at *m/z* 561 and 823 corresponding to $[Pd(Ph(CH)_3Ph)(PPh_3)]^+$ and $[Pd(Ph(CH)_3Ph)(PPh_3)_2]^+$, respectively, were revealed from the ESI(+)-MS analysis of a stoichiometric mixture of **1** and $Pd(PPh_3)_4$ in $MeOH/H_2O$ (entry 11), these clusters probing the in situ formation of η^3-allyl complexes (eq 4).



(4)

From the above ESI-MS analysis, it appears that the classical (η^3-allyl)palladium intermediate is absent from both **1**/**2**/$\mathbf{L_H}$ and **1**/**acacH**/M_2CO_3/**2**/$\mathbf{L_H}$ (M = K, Na) aqueous mixtures. In addition, a mixture of **2**, $\mathbf{L_H}$, and K_2CO_3 in $MeOH/H_2O$ heated to 50 °C led to black particles, due to the reduction of Pd^{II} species,[13] while such particles were not observed in the course of the palladium-mediated reaction depicted in eq 1. Since the reaction time to obtain the full consumption of **1** under the reaction conditions depicted in eq 1 was independent of the presence of palladium, this latter species is not a catalyst of the acetate anion displacement. In contrast, the **3** selectivity was increased from 40 to 92% under the Pd^{II} conditions. Ether **4** is not an intermediate in the formation of **3**, since its conversion was lower than 5% when subjected to the Pd-catalyzed conditions for 24 h. Without palladium, the selectivity depends on the relative nucleophilicity and stability of the potassium enolate, **acacK**, and potassium methanolate, **MeOK**, in the aqueous medium. The high selectivity of the reaction carried out in $MeOH/H_2O$ in the presence of **2** and $\mathbf{L_H}$ is probably connected to the formation of the palladium enolate complex $\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac}$, which could be a more effective nucleophile than **acacK** and **MeOK**. We have also observed that the selectivity decreased strongly when the Pd-catalyzed reaction was carried out in MeOH instead of $MeOH/H_2O$ (eq 5):



(5)

the ether **4** and alcohol **5** were isolated in addition to **3**. As observed in the metal-free process,[2] water favors the formation of **3** and the corresponding process may be described as shown in Scheme 1, which involves the nucleophilic attack of $\mathbf{L_H}{}^\frown\mathbf{PdX}{}^\frown\mathbf{acac}$ on the water-activated substrate. We should point out that, in this scheme, $\mathbf{L_H}$ may be exchanged for the corresponding mono (or multi)-deprotonated ligand.

To test the potential of $\mathbf{L_H}$ as a hydrophilic ligand for the immobilization of palladium, catalytic amounts of $\mathbf{L_H}$ and **2** (0.05 equiv of each) were first reacted with **1** and 2 equiv of both **acacH** and K_2CO_3 in $MeOH/H_2O$ at 50 °C for 24 h. Extraction of the mixture by CH_2Cl_2 and separation of the organic phase yielded 90% of **3**. Successive recycling experiments performed using the recovered aqueous phases afforded **3** in 85, 84, 85, and 85% yield. All of these runs provided slight traces of the ether **4**. These results led us to assume that a Pd^{II} complex is truly immobilized in water by means of $\mathbf{L_H}$.

In conclusion, the present study has revealed the surprising role of a Pd^{II} salt in the allylic substitution reaction of 1-acetoxy-1,3-diphenylpropene with acetylacetone carried out in an aqueous medium. ESI-MS studies have not allowed the observation of an (η^3-allyl)-palladium intermediate but have demonstrated the formation of a palladium acetylacetonate complex. This enolate would react with the substrate to afford 3-(1,3-diphenyl-2-propenyl)-2,4-pentanedione through a highly selective reaction which involves a dramatic role of water. Ligand $\mathbf{L_H}$ is also adapted for the immobilization of Pd^{II} in water, since recycling experiments have been carried out without noticeable loss of activity.

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Supporting Information Available: Figures giving observed electrospray mass spectra and calculated isotopic distribution of all detected species tabulated in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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