Substitution of allylic acetates with sodium *para*-toluenesulfinate in aqueous media using allylpalladium chloride dimer and a water-soluble ligand as the catalytic system; electrospray ionisation mass spectrometry analysis†

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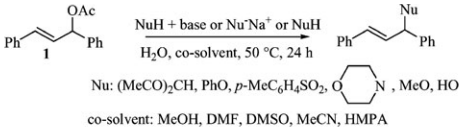
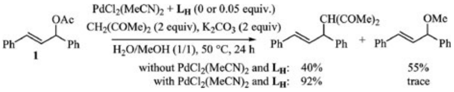
The allylic substitution of allylic acetates by sodium *para*-toluenesulfinate in aqueous media was catalyzed by $[(\eta^3\text{-allyl})PdCl]_2$ associated with $[(HOCH_2CH_2NHCOCH_2)_2NCH_2]_2$. High yields could be obtained but the recycling of the catalytic system proved to be weakly effective. ESI-MS analysis has led to the suggestion of a possible catalytic cycle involving a Pd^{IV} intermediate.

1. Introduction

Nowadays, chemistry that takes place in water receives considerable attention for environmental, economic and safety reasons, and also for showing unique reactivities and selectivities that are not seen in organic solvents.[1] In recent years, we have been involved in this research topic.[2–5] In particular, we have disclosed the water-promoted allylic substitution of (*E*)-1-acetoxy-1,3-diphenylpropene (**1**) by various nucleophiles at 50 °C in the absence of palladium complexes[3] (eqn. (1)) and, with acetylacetonate anion as the nucleophilic species, the unusual role of $PdCl_2(MeCN)_2/L_H$ in the formation of PhCH(CH(COMe)$_2$)CH=CHPh[4] (eqn. (2) (L_H = $[(HOCH_2CH_2NHCOCH_2)_2NCH_2]_2$). The allylic substitution of (*E*)-3-phenyl-1-*para*-tolylallyl acetate by C-, O-, S- and N-nucleophiles also occurred effectively in the absence of a metal catalyst[3] but the reactivity of (*E*)-4-phenylbut-3-en-2-yl acetate (**2**) was much lower.[6] The results obtained from **2** and a range of other allylic acetates are described here, with an electrospray ionisation mass spectrometry (ESI-MS) investigation suggesting mechanistic possibilities.



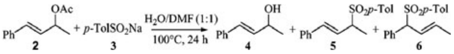
(1)



(2)

2. Results and discussion

Treating **2** with 1.1 equiv. of sodium *para*-toluenesulfinate (**3**) in a 1 : 1 mixture of H_2O and DMF at 100 °C for 24 h led to a 55% conversion of **2**, with the appearance of 4-phenylbut-3-en-2-ol (**4**) (33%), and adducts **5** and **6** (20%, **5**/**6** ratio = 1 : 1) (eqn. (3)). With 2 equiv. of **3**, complete conversion of **2** took place and the yield of the adducts increased to 41%. Decreasing the reaction temperature afforded lower conversions, as exemplified in Fig. 1; no reaction occurring below 60 °C. At 100 °C, switching from **3** to morpholine or $CH_2(COMe)_2$/K_2CO_3 as the nucleophilic species led only to the formation of **4**.



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The above low selectivities and reactivities led us to examine the influence of a Pd catalyst using our previously reported

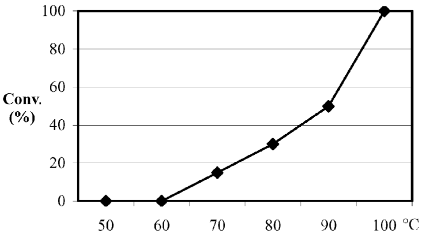

Fig. 1 Influence of reaction temperature on the conversion of **2** in the absence of a Pd catalyst. Experimental conditions: **2** (0.8 mmol), **3** (2 equiv.), H_2O (1 mL), DMF (1 mL), 3 h.

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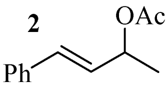
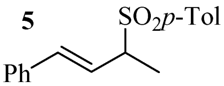
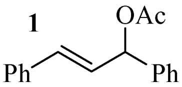
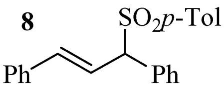
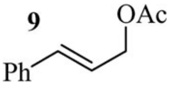
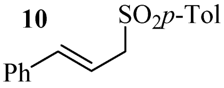
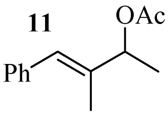
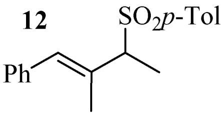
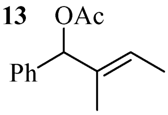
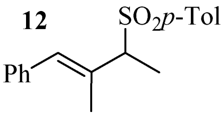
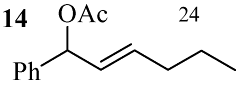
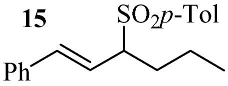
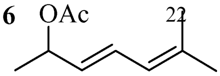
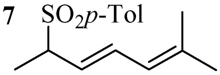
† Electronic supplementary information (ESI) available: Observed electrospray mass spectra and calculated isotopic distribution of the detected species (Fig. S1–S5). See DOI: 10.1039/b613562e

Table 1 Substitution of allylic acetates with **3** in H_2O/MeOH in the presence of $[(\eta^3\text{-allyl})PdCl]_2/L_H$. Experimental conditions: Substrate (1.0 mmol), **3** (2 equiv.), **7** (0.01 equiv.), L_H (0.02 equiv.), H_2O (1 mL), MeOH (1 mL), 50 °C

Entry	Substrate	Time/ h	Product	Yield (%)
1	**2** 	3	**5** 	98
2	**1** 	3	**8** 	99
3	**9** 	3	**10** 	99
4	**11** 	24	**12** 	99
5	**13** 	48	**12** 	22
6	**14** 	24	**15** 	59
7	**16** 	22	**17** 	55

aqueous conditions.[3,4] In contrast to the results produced with **1** as the substrate, the nucleophilic addition of **3** to **2** did not occur at 50 °C using $PdCl_2(MeCN)_2/L_H$ as the catalyst and H_2O/MeOH as the solvent. Gratifyingly though, a mixture of $[(\eta^3\text{-allyl})PdCl]_2$ (**7**) and L_H proved to be an efficient and selective catalytic system in H_2O/MeOH, even at 50 °C, affording a 98% yield of **5** in 3 h (Table 1, entry 1). Similar yields were obtained using DMF, MeCN and HMPA as the co-solvent, while DMSO and THF were less effective (Fig. 2). A high (98%) selectivity was also observed using only water as solvent but the conversion dropped to 68%. As above, the substitution of **2** by morpholine, or the sodium salt of acetylacetone or dimethylmalonate did not occur under these Pd-catalyzed conditions.

Following these observations, a range of allylic acetates were subjected to a **7**/L_H-catalyzed reaction with **3** in H_2O/MeOH. As shown by the results collected in Table 1, the substitution occurred in all cases on the less crowded carbon.

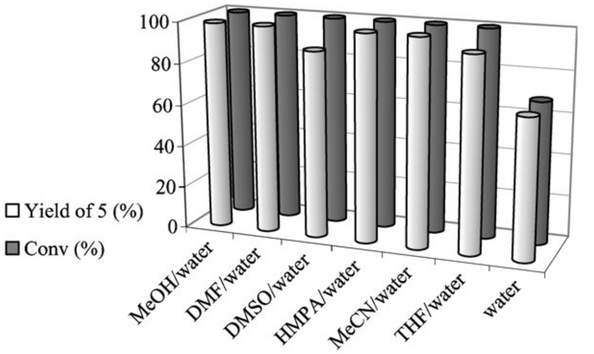


Fig. 2 Reaction of **2** with **3** using $[(\eta^3\text{-allyl})PdCl]_2/L_H$ as the catalyst in various aqueous mixtures. Experimental conditions: **2** (1 mmol), **3** (2 equiv.), **7** (0.01 equiv.), L_H (0.02 equiv.), H_2O (1 mL), co-solvent (1 mL), 50 °C, 3 h.

The fact that isomeric allylic acetates **11** and **13** afford the same product (**12**; Table 1, entries 4 and 5) indicates that **11** and **13** operate through the same allylic intermediate. Substitution of the central atom of the allylic moiety strongly decreased the reaction rate (Table 1, entries 1 and 4). According to the high difference of reactivity between **11** and **13** (Table 1, entries 4 and 5), it also appears that the facility to form the reactive intermediate greatly depends on the structure of the substrate.

A point of interest in metal-catalyzed reactions in aqueous media is the possibility of recycling. To clarify this issue, a reaction carried out as indicated in Table 1, entry 1, was extracted with CH_2Cl_2. After addition of MeOH, **2** and **3** to the aqueous phase, followed by heating at 50 °C, 5 h was required for the complete consumption of **2**, providing **5** in 98% yield. A second recycling was much more sluggish, affording no more than 40% conversion in 24 h.

To obtain information about the mechanism of these reactions, an ESI-MS analysis was undertaken.[7] Each component of the catalytic system was first analyzed. Because Pd and Cl display 6 and 2 isotopes, respectively, the ions containing these isotopes should be mass-detected as clusters of isotopomeric ions whose center depends on the most abundant isotope (106 for Pd and 35 for Cl).

The ESI(+)-MS of **7** in a MeOH/H_2O/THF (5 : 5 : 1) mixture showed three main peaks at m/z = 389, 461 and 513, corresponding to $[(PdC_3H_5Cl)_2 + Na]^+$, $[(PdC_3H_5Cl)_2 + THF + Na]^+$ and the trinuclear metal cluster $[(PdC_3H_5Cl)_3 - Cl]^+$, respectively (Fig. S1, ESI†). Two cationic forms of L_H at m/z = 465 ($[L_H + H]^+$) and 487 ($[L_H + Na]^+$) were observed from the ESI(+)-MS of L_H in MeOH/H_2O (Fig. S2, ESI†). The ESI(+)-MS of an 1 : 2 mixture of **7** and L_H in MeOH/H_2O revealed a peak at m/z = 611 corresponding to $[L_HPdC_3H_5]^+$ (Fig. S3, ESI†). The addition of allylic acetate **2** (2.0 equiv. with respect to **7**) to this **7** + L_H mixture did not afford new peaks. The ESI(+)-MS spectra only evolved after the addition of sulfinate **3** (4 equiv./**7**); after one hour at 50 °C, besides the previous $[L_HPdC_3H_5]^+$ peak, peaks at m/z = 701 and 879 were obtained. Peak m/z = 701 is attributable to $[L_HPd(\mathbf{2}) - OAc]^+$ while m/z = 879 is consistent with $[L_HPd(\mathbf{2})SO_2p\text{-Tol} - OAc + Na]^+$ and $[L_HPd(\mathbf{5}) + Na]^+$ (Fig. 3 and Fig. 4). After 24 h, the mixture was extracted with

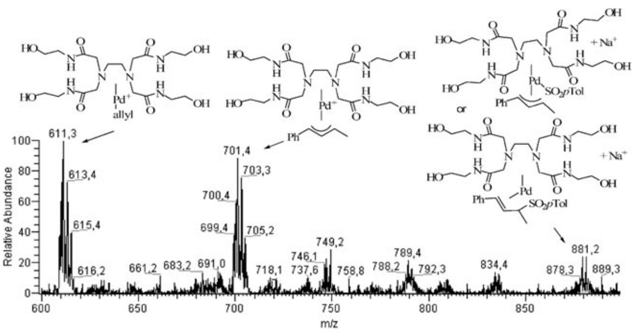


Fig. 3 ESI(+)-MS spectrum of the crude mixture obtained under the following conditions: **7**, L_H (2 equiv.), **2** (2 equiv.), **3** (4 equiv.), H_2O/MeOH (1 : 1), 50 °C, 1 h.

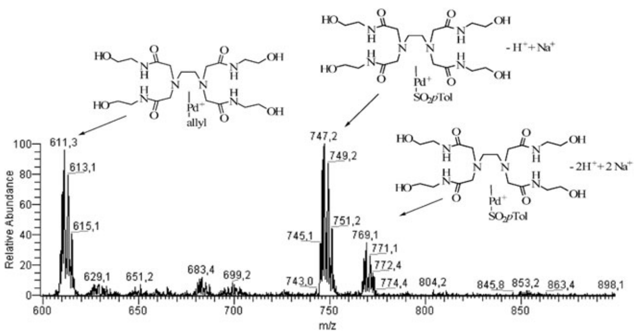


Fig. 5 ESI(+)-MS spectrum of the aqueous phase after extraction of the crude mixture with CH_2Cl_2. Experimental conditions: As in Fig. 3 for 24 h followed by extraction with CH_2Cl_2.

CH_2Cl_2 and the ESI(+)-MS spectrum of the aqueous phase recorded. This spectrum showed the peak at m/z = 611 already observed, and two new clusters centered at m/z = 747 and 769, attributable to $[L_HPdSO_2p\text{-Tol} - H + Na]^+$ and $[L_HPdSO_2p\text{-Tol} - 2H + 2Na]^+$ (Fig. 5; Fig. S4, ESI†).

Further ESI-MS experiments were carried out using either $CH_2(COMe)_2$ + K_2CO_3 or $NaCH(COMe)_2$. In the first case (Fig. S5, ESI†), we only observed $[L_HPdC_3H_5]^+$ and $[L_HPdC_3H_5 - H + K]^+$ clusters. The use of $NaCH(COMe)_2$ led similarly to $[L_HPdC_3H_5]^+$ and $[L_HPdC_3H_5 - H + Na]^+$ clusters but, in addition, to traces of $[L_HPd(\mathbf{2}) - OAc]^+$ (Fig. S6, ESI†). These ESI-MS analyses, which are in agreement with the reactivity of the sulfinate anion and the reluctant addition of acetylacetonate anion highlighted in the preparative experiments, have lead us to make mechanistic proposals for the allylic substitution of **2** by **3** under these particular Pd-catalyzed conditions.

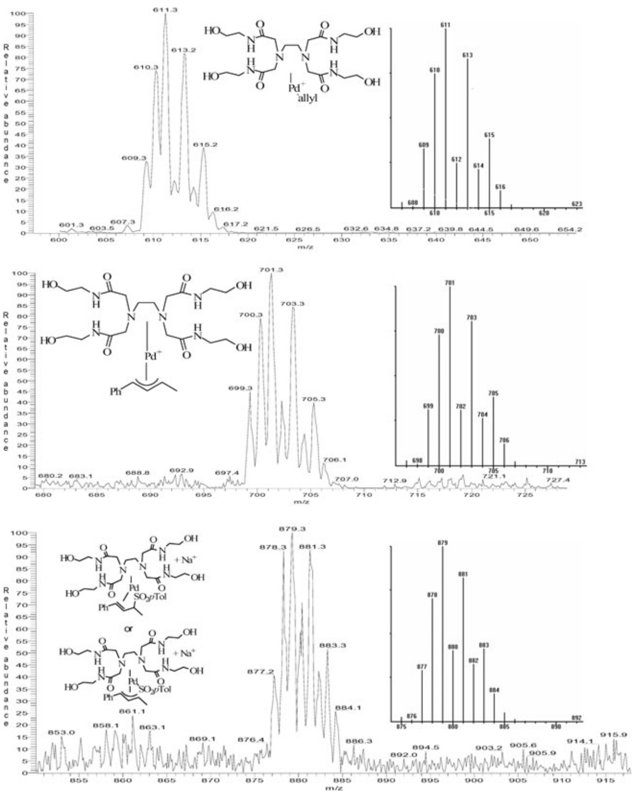
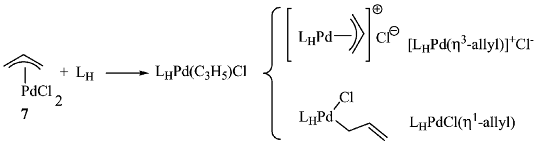


Fig. 4 Expanded ESI(+)-MS spectra of detected species from Fig. 3 and corresponding theoretical spectra.

Mixing **7** with L_H led to a monomeric η^3- or η^1-allylpalladium complex, having L_H as a bidentate ligand, namely $L_HPd(C_3H_5)Cl$, revealed by the cluster $[L_HPdC_3H_5]^+$. This complex is either cationic with an η^3-allyl moiety, or neutral with an η^1-allyl moiety (Scheme 1). Let us now to consider two possible mechanisms, **A** and **B**, that could explain the reactivity of these species in the presence of **3** and **7**.



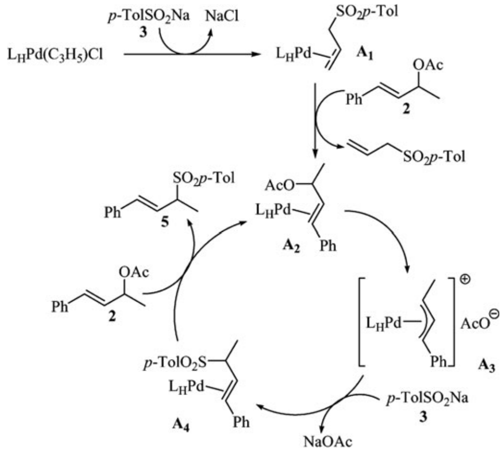
Scheme 1

Mechanism A

Mechanism **A** is similar to the catalytic cycle usually described for Tsuji–Trost reactions using a mixture of **7** and a phosphine as the catalyst (Scheme 2). Pd^0 complex $\mathbf{A_1}$ arises from the nucleophilic addition of **3** to $L_HPd(C_3H_5)Cl$. An exchange of ligand with **2** leads to $\mathbf{A_2}$ and then to cationic Pd^{II} complex $\mathbf{A_3}$. The reaction of **3** with $\mathbf{A_3}$ affords Pd^0 complex $\mathbf{A_4}$, which evolves to $\mathbf{A_2}$, closing the catalytic cycle.

Intermediates $\mathbf{A_2}$ and $\mathbf{A_3}$ are consistent with the cluster at m/z = 701, attributed to $[L_HPd(\mathbf{2}) - OAc]^+$, while $\mathbf{A_4}$ is in agreement with the cluster at m/z = 879. In contrast, mechanism **A** is not in accordance with the ESI-MS spectrum recorded at the end of the reaction, which highlights a cluster at m/z = 611 corresponding to the complex $L_HPd(C_3H_5)X$ (X = Cl, OAc or SO_2p-Tol). To accept mechanism **A**, it is a required consideration that only a slight portion of $L_HPd(C_3H_5)Cl$ reacts with **3**. $L_HPd(C_3H_5)Cl$ would act as a reservoir of Pd^{II}, which is reduced to Pd^0 to enter the catalytic cycle. However the need for an explanation remains as to why **3** would react with $\mathbf{A_3}$ rather than with $L_HPd(C_3H_5)Cl$.

Since 2 equiv. per Pd of polydentate ligand L_H are used, according to the research groups of Shaw and Jutand,[8–11] the



Scheme 2

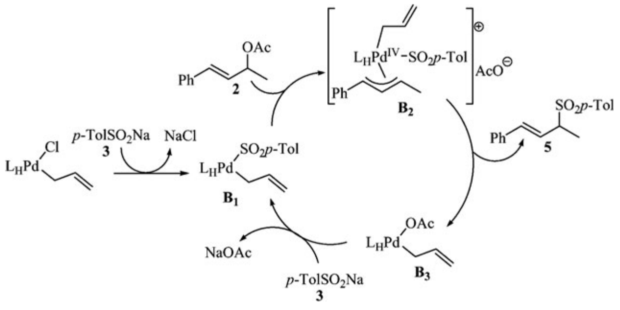
most likely form of the allyl moiety of a species such as $L_HPd(C_3H_5)Cl$ is the η^1-allyl one.[12] Consequently, this species would be the neutral complex $L_HPdCl(\eta^1\text{-allyl})$ (Scheme 1). As a cationic palladium complex is more reactive towards nucleophilic addition than a neutral one,[10] this could explain the reaction of **3** with the cationic complex $\mathbf{A_3}$ rather than with $L_HPdCl(\eta^1\text{-allyl})$.

Mechanism B

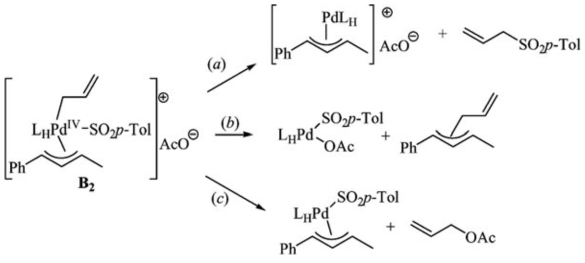
For mechanism **B**, we take into consideration (i) the most likely structure of $L_HPd(C_3H_5)Cl$,[8–11] *i.e.* the neutral complex $L_HPdCl(\eta^1\text{-allyl})$, (ii) the reported substitution at Pd of chloropalladium complexes with $PhSO_2Na$,[13] and (iii) Kurosawa's proposal of a reductive elimination leading to an R-allyl from $Pd^{IV}(allyl)_2R(X)PPh_3$.[14]

An exchange of anion between $L_HPdCl(\eta^1\text{-allyl})$ and **3** affords $\mathbf{B_1}$ (Scheme 3). Such a step could be considered a transmetallation. The reaction of $\mathbf{B_1}$ with **2** leads to cationic Pd^{IV} complex $\mathbf{B_2}$.[15] Kurosawa *et al.* have shown that reductive elimination was more efficient from an η^3-allyl than from an η^1-allylpalladium complex.[17–19] Consequently, reductive elimination from $\mathbf{B_2}$ produces **5** rather than allylSO$_2$*p*-Tol. Such an elimination results in $\mathbf{B_3}$, which interacts with **3** to close the catalytic cycle.

According to mechanism **B**, the real catalyst is $L_HPd(SO_2p\text{-Tol})(\eta^1\text{-allyl})$ ($\mathbf{B_1}$). $\mathbf{B_1}$ is consistent with the cluster at $m/z = 611$, corresponding to $[L_HPdC_3H_5]^+$, which has been observed in both the crude mixture and the aqueous extraction phase. Pd^{IV} complexes have been isolated[20] but the formation of a Pd^{IV} complex from a Pd^{II} complex and an allylic acetate, *i.e.* in Scheme 3 the formation of $(\eta^1\text{-allyl})(\eta^3\text{-allyl})Pd^{IV}$ species $\mathbf{B_2}$ from **2** and $(\eta^1\text{-allyl})Pd^{II}$ intermediate $\mathbf{B_1}$, is an unusual step. Nevertheless, Kurosawa's team have (i) already suspected a Pd^{IV} intermediate from the oxidative addition of allyl acetate to an $(\eta^3\text{-allyl})Pd^{II}$ complex[14] and (ii) shown that $(\eta^1\text{-organo})metal^{II}$ complexes are more similar to $metal^0$ than $metal^{II}$ complexes.[21] In addition, the formation of a cationic $(\eta^3\text{-allyl})Pd^{IV}$ intermediate has recently been proposed for the reaction of a vinylpalladium chloride with an allylic alcohol in an aqueous medium.[22]



Scheme 3



Scheme 4

The clusters at $m/z = 701$, 747, 769 and 879 are not directly consistent with the intermediates of mechanism **B** but can be connected to $\mathbf{B_2}$ through the reactions depicted in Scheme 4. Indeed, the cluster at $m/z = 701$ corresponds to $[L_HPd(PhC_3H_3Me)]^+$ while those centered at $m/z = 747$ and 769 occur from $[L_HPdSO_2p\text{-Tol}]^+$. These species would arise from reductive eliminations (paths (a)[23] and (b)[24]) less favored than the one depicted in Scheme 3. The cluster at $m/z = 879$ can be produced not only from $L_HPd(\mathbf{5})$ (intermediate $\mathbf{A_4}$ in Scheme 2) but also from $\mathbf{B_2}$ *via* the nucleophilic addition of acetate anion to the η^1-allyl ligand (path (c)), *i.e.* a reaction already documented for a cationic $(\eta^1\text{-allyl})$palladium complex.[25–27] Steps (a), (b) and (c) would produce minute amounts of organic compounds since the C_3H_5 moiety comes from the catalyst. Furthermore, step (c), which leads to allyl acetate, would be reversible.

A possible explanation for the unreactivity of morpholine, and the sodium salts of acetylacetone and dimethylmalonate, involves the influence of steric effects.[26,33] L_H is a crowded ligand and, according to mechanism **B**, the sulfinate group is a ligand of palladium before being linked to the allyl moiety. Consequently, the size of the nucleophilic species could play a decisive role. Mechanisms **A** and **B** remain, nevertheless, hypothetical but we have, however, to point out that the extracted aqueous phase contains $L_HPdX(allyl)$. Such a species, namely $\mathbf{B_1}$, is directly involved in mechanism **B**, and we have obtained **5** in 98% yield from a preparative experiment using a recycled aqueous phase.

3. Conclusion

A mixture of both $[(\eta^3\text{-allyl})PdCl]_2$ and a water soluble ligand catalyzes the allylic substitution of allylic acetates by sodium *para*-toluenesulfinate in a variety of aqueous media, but the system quickly looses its catalytic properties upon recycling.

Substitution of the allylic moiety of the substrate has a significant influence on the efficiency of the reaction. ESI-MS analyses have led to the suggestion of a possible catalytic cycle involving a Pd^{IV} intermediate.

4. Experimental

3.1. General procedure for Pd-catalyzed substitution

To a mixture of $[(\eta^3\text{-allyl})PdCl]_2$ (3.6 mg, 0.01 mmol) and $[(HOCH_2CH_2NHCOCH_2)_2NCH_2]_2$ (9.3 mg, 0.02 mmol) in MeOH (1 mL), stirred at room temperature for 1 h, was added the substrate (1.0 mmol), sodium *para*-toluenesulfinate (388 mg, 2 mmol) and H_2O (1 mL). After heating at 50 °C for the time indicated in Table 1, the organic compounds were extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated to give the crude product. This product was purified by chromatography over silica gel eluted with a 10 : 90 mixture of AcOEt and petroleum ether.

3.2. ESI-MS analysis

ESI-MS 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 negative ESI(−) ion mode at a probe tip voltage of 3 kV. 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 $\mu L\ min^{-1}$ 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 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 using the Isoform program and were used to aid assignment. Association of the substrate with ions was common. $[M + H]^+$ and $[M + Na]^+$ were often observed, the latter appeared from reactions with traces of cations present, even in HPLC-grade solvent.[7]

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