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# Synthesis and structural features of α-acyloxy-(η³-allyl)palladium complexes

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**Abstract**

α-Acetoxy (η³-allyl)palladium complexes were prepared from acyloxy functionalized allylsilanes under mild conditions and in good isolated yields. The substituent and ligand effects of the acetoxy group on the palladium–allyl bonding were studied by X-ray diffraction. These studies show that the acetoxy group generates a strongly deformed bonding between the metal atom and the allyl moiety. This unsymmetrical bonding is modulated by the σ-donor/π-acceptor properties of the ligands. The $^{13}C$ NMR studies indicated that the shift values correlate with the carbon–palladium bond lengths and the inductive effects of the acetoxy group.


*Keywords:* Allyl; Palladium, Ligand effects; Carbon–metal bonding; X-ray structure

## 1. Introduction

Allylpalladium chemistry offers efficient and selective preparative methods for synthesis of densely functionalized allylic products [1–4]. In these reactions allylpalladium complexes occur as catalytic intermediates, which are usually generated by the displacement of the allylic leaving group (e.g. acetate, carbonate, carbamate or halide) by a palladium(0) catalyst [1–8]. Alternatively, allylpalladium intermediates can be formed by reaction of palladium(II) catalysts with alkenes [9–13], dienes [14–17] and allylsilanes [18–27]. Under appropriate conditions the resulted (η³-allyl)palladium intermediates react with a wide range of nucleophiles, such as malonates, enolates, and different N- and O-nucleophiles [1–4]. The regiochemistry of the nucleophilic attack on the (η³-allyl)palladium complexes is mainly determined by the electronic and steric effects of the allylic substituents [1–8,28,29]. Therefore, explicit knowledge on the effects of the allylic substituents on the structure of (η³-allyl)palladium complexes is indispensable for development of new selective palladium-catalyzed transformations.

In this paper we report our recent results on preparation and structural studies of α-acyloxy (η³-allyl)palladium complexes (**1a**–**g**). These types of complexes are reaction intermediates in important palladium-catalyzed allylic substitution reactions [30–34], in which the regioselectivity of the reaction is controlled by the electronic effects of the acyloxy substituent. Interestingly, the nucleophilic attack on α-acyloxy (η³-allyl)palladium intermediates usually takes place at the acyloxy substituted carbon to give the branched allylic product [30–33], while the regioselectivity of the catalytic transformations via β-acyloxy (η³-allyl)palladium intermediates is reversed to give the linear allylic product [14,28,35–38]. Although, several studies have appeared on the β-substituent effects in (η³-allyl)palladium complexes, the α-substituent effects received somewhat less attention. Therefore, in the present study we concentrated to the substituent effects of the acyloxy substituent on the structure of (η³-allyl)palladium complexes using X-ray crystallography and $^{13}C$ NMR spectroscopy.

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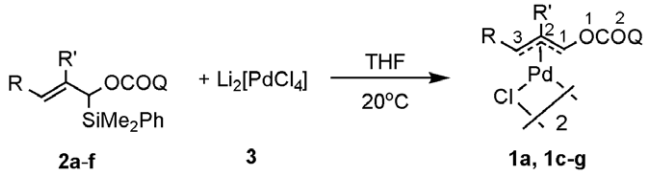
## 2. Results and discussion

As mentioned above there are two main strategies for preparation of functionalized ($\eta^3$-allyl)palladium complexes by allylic displacement of the appropriate leaving group by palladium. The first method is based on the reaction of palladium(0) complexes with allyl acetates or chlorides [39,40] This method was employed by Åkermark and co-workers [41] to synthesize an α-acetoxy ($\eta^3$-allyl)palladium complex, which has been the only one described in the literature so far. An alternative method for synthesis of ($\eta^3$-allyl)palladium complexes is based on use of palladium(II) sources and functionalized allylsilanes [20,23,42]. We employed this latter method for synthesis of α-acyloxy ($\eta^3$-allyl)palladium complexes because of its efficiency and high functional group tolerance. Accordingly, various allylsilanes **2a**–**2f**, prepared using the method reported by Panek and Sparks [43], were reacted with $Li_2[PdCl_4]$ (**3**) in THF to obtain chloro-dimer complexes **1a** and **1c**–**g** in good yield (Scheme 1 and Table 1). The palladadesilylation reaction of allylsilanes **2a**–**b** and **2d**–**f** was accomplished in 2–3 h under mild conditions. However, in the presence of an electron supplying *p*-methoxy-benzoyl group (**2c**) formation of the corresponding ($\eta^3$-allyl)palladium complex (**1d**) is relatively slow (entry 4). Interestingly, purification of the crude-product obtained from the reaction of **2a** and **3** resulted in two isomeric forms in a ratio of 2.4–1. As the $^1H$ and $^{13}C$ NMR spectrum of these forms are identical within 0.1 ppm and 0.9 ppm, respectively, the two isomers probably differ only in the configuration of their chloro bridges [44]. Phosphine complex **1b** was prepared from **1a** by exchange of the chloro ligand to dppe using $AgBF_4$ (entry 2). The obtained complexes **1a**–**g** proved to be air- and thermo-stable, and therefore they could be purified by column chromatography. The solubility of chloro complexes **1a** and **1c**–**g** is relatively low in common organic solvents, and therefore their $^{13}C$ NMR spectrum was recorded in DMSO-$d_6$. On the other hand, phosphine complex **1b** is easily soluble in most organic solvents, however, it was decomposed in DMSO, and therefore a $CDCl_3$ solution was used for determination of the NMR spectrum.




Scheme 1.

*Comparison of the X-ray structure of **1a** and **1b**.* In order to determine the substituent effects of the acetoxy substituent on the structure of chloride and dppe ligated ($\eta^3$-allyl)palladium complexes, we carried out single-crystal X-ray diffraction measurements. In both complexes the acetoxy group is co-planar with the allyl-plane (Fig. 1) indicating a conjugative interaction between the acetoxy group and the π-system of the allyl moiety. Inspection of Fig. 1 reveals that the carbon–palladium bonds are systematically shorter in **1a** than in **1b**. This is a well-known structural effect of the σ-donor chloride anion on the bonding structure of ($\eta^3$-allyl)palladium complexes [37,45,46]. Interestingly, in **1a** the Pd–C3 bond (2.137 Å) is longer than the Pd–C1 bond (2.074 Å) by 0.06 Å. On the contrary, in phosphine complex **1b** the Pd–C3 bond (2.156 Å) is shorter than the Pd–C1 bond (2.212 Å) by 0.06 Å, and thus the Pd–C1 bond in **1b** is longer than the corresponding palladium–carbon bond in **1a** by 0.14 Å. As a consequence of the unsymmetrical palladium–allyl bonding in **1a** and **1b**, the oxygen atom of the acetoxy group (O1) is much closer to palladium in **1a** (2.963 Å) than in **1b** (3.205 Å). The above described perturbation of the acyloxy group on the palladium–allyl bonding is very similar to the substituent effects of other functionalities [28,37,38,45–47], however, the magnitude observed for **1a** and **1b** is clearly the largest.

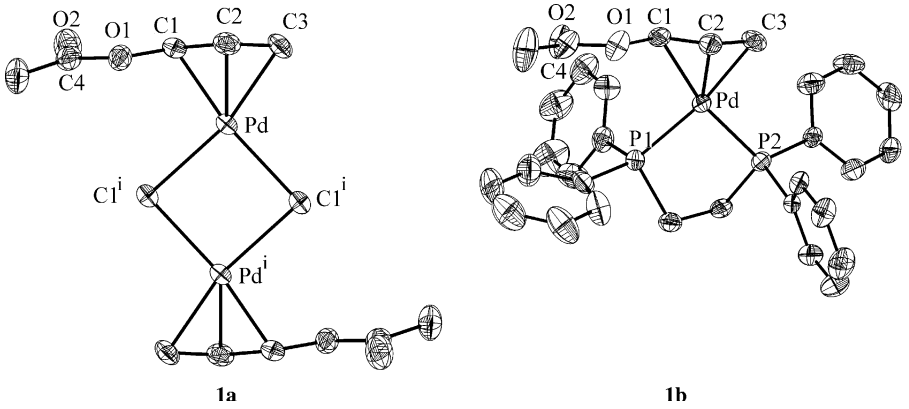



Fig. 1. X-ray structure of Complexes **1a** and **1b**. Selected bond lengths (Å) for **1a**: Pd–C1, 2.074(5); Pd–C2, 2.079(4); Pd–C3, 2.137(4); C1–C2, 1.383(7); C2–C3, 1.359(7); C1–O1, 1.405(8); C4–O1, 1.345(6); C4–O2, 1.194(5); Pd–Cl1, 2.4301(14); Pd–Cl1$^i$, 2.3973(16) (symmetry code i = $-x$, $1-y$, $1-z$). Selected bond lengths (Å) for **1b**: Pd–C1, 2.212(6); Pd–C2, 2.158(7); Pd–C3, 2.156(7); C1–C2, 1.390(8); C2–C3, 1.375(10); C1–O1, 1.410(8); C4–O1, 1.362(8); C4–O2, 1.177(9); Pd–P1, 2.2951(16); Pd–P2, 2.3066(18).