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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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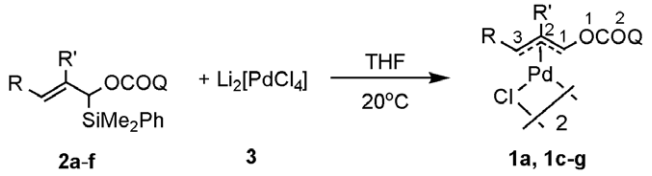
2. Results and discussion

As mentioned above there are two main strategies for preparation of functionalized (η^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 (η^3-allyl)palladium complex, which has been the only one described in the literature so far. An alternative method for synthesis of (η^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 (η^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 (η^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 (η^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 (η^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.

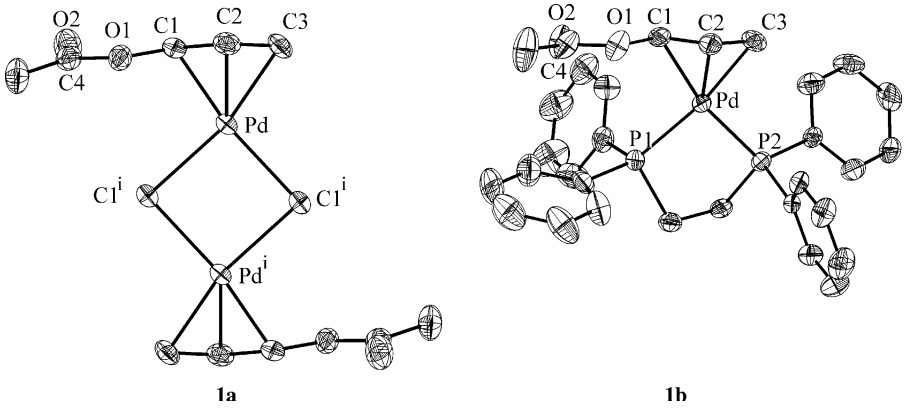
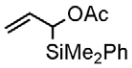
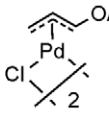
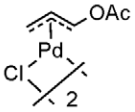
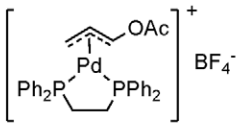
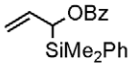
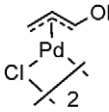
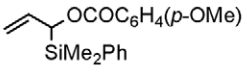
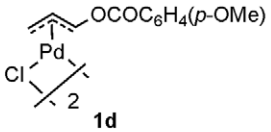
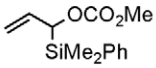
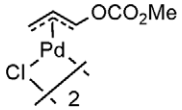
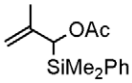
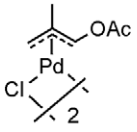
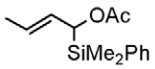
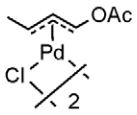


Fig. 1. X-ray structure of Complexes **1a** and **1b**. Selected bond lengths (Å) for **1a**: Pd–C1, 2.074(5); Pd–C2, 2.079(4); Pd–C3, 2.137(4); C1–C2, 1.383(7); C2–C3, 1.359(7); C1–O1, 1.405(8); C4–O1, 1.345(6); C4–O2, 1.194(5); Pd–Cl1, 2.4301(14); Pd–Cl1^i, 2.3973(16) (symmetry code i = $-x$, $1-y$, $1-z$). 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).

Table 1
Synthesis of α-acyloxy (η^3-allyl)palladium complexes

Entry	Substrate	Method[a]	Cond.[b]	Product	Yield[c]
1	 **2a**	A	20 / 3	 **1a**	68
2	 **1a**	B	0 / 0.5	 **1b**	95
3	 **2b**	A	20 / 2	 **1c**	63
4	 **2c**	A	20 / 6	 **1d**	71
5	 **2d**	A	20 / 3	 **1e**	57
6	 **2e**	A	20 / 3	 **1f**	50
7	 **2f**	A	20 / 3	 **1g**	67

[a] Method A: The reactions were conducted in THF using $Li_2[PdCl_4]$ (**3**) as palladium source. Method B: The chloride to dppe ligand exchange was mediated by $AgBF_4$ in $CHCl_3$.
[b] Reaction temperature/reaction time (°C)/(h).
[c] Isolated yield.

^{13}C NMR shifts of the allylic carbons. It is well known [48,49] that ^{13}C NMR shift values of the allylic carbons are strongly influenced by the substituent and ligand effects. Accordingly, the acetoxy substituted C1 carbon in **1b** (108.9 ppm) is less shielded (Table 2) than the corresponding carbon in **1a** (105.4 ppm). This effect is probably due to the longer Pd–C1 bond in **1b** than in **1a** (Fig. 1), which leads to less shielding by the electropositive palladium on C1 in **1b** than in **1a**. Varying the acyl substituent (Q) has a relatively weak effect on the chemical shift of C1.

The methoxy substitution of the benzoyl group has a small but significant effect, as C1 in the methoxy benzoyl derivative **1d** (105.8 ppm) is somewhat more shielded than the C1 in **1c** (106.1 ppm). There is large difference (typically 43–44 ppm) in the shift values of C1 and C3 carbons, because of the inductive effects of the acyloxy substituents. Interestingly, substitution of C2 (**1f**) leads to a decrease of the difference of the shift values of the allylic terminal carbons (37 ppm). It is particularly interesting to compare the substituent effects of the methyl and acetoxy groups on the terminal carbons in **1g**. The shielding value at the methyl substituted allylic terminus (C3) is 81.9 ppm, which is very similar to the shift value observed for the simple methyl–allyl complex analog [48] (81.5 ppm). On the other hand,

Table 2
^{13}C NMR shifts (δ) of the allylic carbons (ppm)[a]

	C1	C2	C3
1a	105.4	104.1	61.7
1b	108.9	110.3	61.6
1c	106.1	103.9	61.5
1d	105.8	104.4	61.2
1e	106.0	105.7	61.3
1f	100.8	120.6	63.1
1g	106.9	100.1	81.9

[a] The spectrum of **1b** is recorded in $CDCl_3$, while rest of the spectra are recorded in DMSO-d_6.

the acetoxy substituted C1 (106.9 ppm) in **1g** is much more deshilded than C3 (81.9 ppm) indicating that the inductive effect of the acetoxy group is much stronger than that of the methyl group in the allyl moiety. This inductive effect may explain the preferential attack at the acetoxy substituted carbon in palladium-catalyzed allylic substitution reactions proceeding via α-acetoxy substituted (η^3-allyl)palladium complexes.

3. Conclusions

α-Acyloxy substituted (η^3-allyl)palladium complexes (**1**) can be simply and efficiently prepared by palladadesilylation of acetoxy allyl silanes. The structural analysis of **1a** and **1b** clearly shows that the acetoxy substituent has a pronounced substituent effect on the allyl moiety. In chloro-complex **1a**, the acetoxy substituted carbon (C1) interacts stronger with palladium than the other terminal carbon (C3). The ligand effects alter the carbon–metal bonding, and thus in dppe complex **1b** the substituted carbon (C1) is less strongly bound to palladium than the unsubstituted one (C3). The substituent effects of the acyloxy groups are similar to other allylic functionalities, however, the substituent effects leads to a considerable deformation of the palladium–allyl bonding. The strong inductive effects of the acyloxy substituents are clearly reflected by the ^{13}C NMR shifts of the complexes. This inductive effect varies relatively weakly with the substituents of the acyloxy group. The acetoxy substitution of the allylic terminal carbon leads to a considerably larger deshilding of (by 25 ppm) than the methyl substitution.

4. Experimental

The THF used in the reactions was distilled over benzophenone/Na prior to use. ^1H NMR spectra were recorded at either 300 or 400 MHz, ^{13}C NMR spectra were recorded at either 75.4 or 100.5 MHz ($\delta(CDCl_3) = 7.26$ ppm and 77.0 ppm, δ(DMSO-d_6) = 2.54 ppm and 40.45 ppm). For column chromatography silica gel (230-400 mesh) was used. The eluent systems are given in volume:volume ratios.

General procedure for preparation of allylpalladium complexes (Method A). The appropriate allylsilane (0.5 mmol) was dissolved in dry THF (5 mL) at 20 °C under argon atmosphere, and then Li_2PdCl_4 (130 mg, 0.5 mmol) was added. The resulting solution was stirred for the time given in Table 1, and then the solvent was evaporated and the crude product was purified by silica-gel chromatography affording the products as pale-yellow powders. The NMR-spectra of the products were recorded in DMSO-d_6 except for complex **1b** which was recorded in $CDCl_3$.

*(η^3-1-Acetoxy-allyl)palladium chloride dimer (**1a**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography using $CHCl_3$ as eluent. On the column, two well separated yellow bands were observed (fraction A and fraction B). The isolated product ratio between fraction A and B was found to be 2.4:1. NMR data for fraction A: ^1H NMR: 2.04 (s, 3H), 3.63 (bs, 2H), 5.98 (q, 1H, $J = 9.8$, 14.0 Hz), 6.98 (d, 1H, $J = 9.0$). ^{13}C NMR: 21.71, 61.66, 104.14, 105.38, 168.47. NMR data for fraction B: ^1H NMR: 2.13 (s, 3H), 3.64 (bs, 2H), 6.05 (q, 1H, $J = 9.9$, 14.9), 7.04 (d, 1H, $J = 9.1$). ^{13}C NMR: 21.70, 61.29, 103.86, 105.06, 168.47. Preparation of crystals for X-ray diffraction: 20 mg of **1a** (from fraction A) was dissolved in 0.5 mL CH_2Cl_2 followed by layering pentane (0.25 mL) on the surface of this solution; and the resulting mixture was kept at 4 °C affording crystals suitable for X-ray diffraction.

*(η^3-1-Benzoyloxy-allyl)palladium chloride dimer (**1c**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography using CH_2Cl_2 as eluent. ^1H NMR: 3.83 (bs, 2H), 6.28 (q, 1H, $J = 9.2$, 15.1 Hz), 7.30 (d, 1H, $J = 9.2$ Hz), 7.59 (t, 2H, $J = 7.4$ Hz), 7.74 (t, 1H, $J = 7.6$ Hz), 8.05 (d, 2H, $J = 8.3$ Hz). ^{13}C NMR: 61.75, 104.08, 106.29, 129.39, 129.71, 130.61, 134.90, 163.85.

*(η^3-1-(4-Methoxy)benzoyloxy-allyl)palladium chloride dimer (**1d**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography using CH_2Cl_2:toluene (5:1) as eluent. ^1H NMR: 3.81 (bs, 1H), 3.89 (s, 3H + 1H), 6.23 (q, 1H, $J = 9.6$, 14.2 Hz), 7.11 (d, 2H, $J = 8.5$ Hz), 7.28 (d, 1H, $J = 9.3$ Hz), 8.00 (d, 2H, 8.5 Hz). ^{13}C NMR: 61.53, 103.86, 106.07, 129.17, 129.49, 130.39, 134.68, 163.63.

*(η^3-1-Methyl carbonate-allyl)palladium chloride dimer (**1e**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography using CH_2Cl_2:toluene (5:1) as eluent. ^1H NMR: 3.74 (bs, 2H), 3.81 (s, 3H), 6.09 (q, 1H, $J = 9.7$, 14.8 Hz), 6.92 (d, 1H, $J = 8.8$). ^{13}C NMR: 56.49, 61.68, 105.74, 105.96, 153.31.

*(η^3-1-Acetoxy-2-methyl-allyl)palladium chloride dimer (**1f**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography using CH_2Cl_2:ether (100:1) as eluent. ^1H NMR: 2.15 (s, 3H + 3H), 3.34 (bs, 1H), 4.01 (bs, 1H), 6.91 (s, 1H). ^{13}C NMR: 18.00, 21.79, 63.11, 100.84, 120.63, 168.48.

*(η^3-1-Acetoxy-3-methyl-allyl)palladium chloride dimer (**1g**)*. This complex was prepared according to method A. The crude product was purified by silica-chromatography

using CH_2Cl_2:ether (100:1) as eluent. ^{1}H NMR: 1.53 (d, 3H, $J = 6.5$ Hz), 2.10 (s, 3H), 4.25 (m, 1H), 6.02 (dd, 1H, $J = 8.8$, 12.2 Hz), 6.90 (d, 1H, $J = 8.6$ Hz). ^{13}C NMR: 17.78, 21.79, 81.88, 100.11, 106.92, 168.79.

*Preparation of complex **1b** (Method B).* Dimer **1a** (25 mg, 0.05 mmol, from fraction A) was dissolved in $CHCl_3$ (0.2 mL) and added slowly to a suspension of diphenylphosphinoethane (dppe) (41 mg, 0.10 mmol) and $AgBF_4$ (20 g, 0.10 mmol) in 0.5 mL $CHCl_3$ at 0 °C under argon. The solution was stirred for 30 min at 0 °C, then the AgCl precipitation was removed by centrifugation and the supernatant was concentrated in vacuo yielding **1b** as a white powder in 95% yield. ^{1}H NMR: 1.43 (s, 1H), 2.18 (m, 2H), 2.94 (m, 2H), 3.07 (t, 1H, $J = 12.1$ Hz), 4.96 (t, 1H, $J = 7.7$ Hz), 6.08 (q, 1H, $J = 9.8$, 16.9 Hz), 7.10 (t, 1H, $J = 10.7$ Hz), 7.16–7.86 (m, 20H). ^{13}C NMR: 19.55, 26.64 (dd, $J = 14.1$, 31.8 Hz), 28.30 (dd, $J = 13.5$, 33.3 Hz), 61.64 (dd, 4.6, 26.9), 103.63 (dd, 8.0, 36.43 Hz), 125–145 (aromatic C), 166.91. Preparation of crystals for X-ray diffraction: Complex **1b** (50 mg) was dissolved in $CHCl_3$ (0.5 mL). To this solution pentane (0.25 mL) was layered and the obtained mixture was kept at 4 °C to form crystals suitable for X-ray diffraction.

*Determination of the X-ray structure of **1a** and **1b**.* The intensities of the reflections were integrated with the STOE software [50], and the numerical absorption correction was performed with the programs X-RED and X-SHAPE. The structure was solved by direct methods (SHELXS-97 [51]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [52]).

*Crystal data for **1a**:* $C_{10}H_{14}Cl_2O_4Pd_2$: $M = 481.95$. Orthorhombic space group, *Pbca* (No. 61), $a = 7.638(2)$ Å, $b = 7.797(2)$ Å, $c = 24.939(11)$ Å, $V = 1485.2(9)$ Å^3, $Z = 4$, $T = 293$ K, $D_{calc} = 2.155$ g cm^{-3}, μ (Mo Kα) = 2.78 mm^{-1}, $F(000) = 929$, 5824 reflections measured, 762 unique ($R_{int} = 0.151$), 712 observed ($I > 2\sigma(I)$), 96 parameters refined, absorption correction (numerical): $T_{min}/T_{max} = 0.269/0.613$. $R_1 = 0.0295$ ($I > 2\sigma(I)$), $wR(F^2) = 0.0754$, $S = 1.12$ (all data). Maximum/minimum residual electron density: 0.81/−0.49.

*Crystal data for **1b**:* $C_{31}H_{30}BF_4O_2P_2Pd$: $M = 689.72$. Hexagonal space group, $P6_1$ (No. 169), $a = 24.182(2)$ Å, $c = 9.8114(6)$ Å, $V = 4968.6(8)$ Å^3, $Z = 6$, $T = 293$ K, $D_{calc} = 1.390$ g cm^{-3}, μ(Mo Kα) = 0.705 mm^{-1}, $F(000) = 2115$, 26 301 reflections measured, 4147 unique ($R_{int} = 0.0977$), 3221 observed ($I > 2\sigma(I)$), 372 parameters refined, absorption correction (numerical): $T_{min}/T_{max} = 0.894/0.917$. $R_1 = 0.0461$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1157$, $S = 1.04$ (all data), absolute structure, Flack parameter = −0.04(6). Maximum/minimum residual electron density: 0.72/−033. Data collection: STOE-IPDS image plate diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å).

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Appendix A. Supporting information

^{13}C NMR spectra for complexes **1a**–**1g**. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 296820 and 296821 for compounds **1a** and **1b**, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.013.

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