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Synthesis of (π-allyl)palladium complexes from cationic palladium(II) complexes and allylic alcohols[☆]

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Abstract

(π-Allyl)palladium(II) complexes can be synthesized from $[PdCl]^+X^-$ (X = OTf or BF_4) and allylic alcohols via pathways involving Pd–OH elimination. © 1999 Published by Elsevier Science S.A. All rights reserved.

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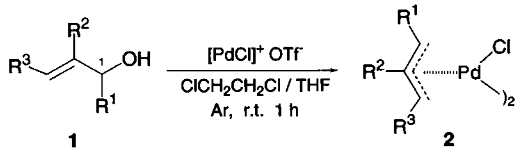
Among the chemistry of (π-allyl)palladium complexes, in situ formation of (π-allyl)palladium complexes from allylic acetates and palladium(0) catalysts [1] is well-documented. In contrast to this, little is known about the formation of (π-allyl)palladium(II) from allylic compounds and palladium(II) salt itself [2,3]. Allyl alcohol (2-propen-1-ol) is known to react with $PdCl_2$ to give (π-allyl)palladium(II) chloride [4]. However, focus on this reaction was directed toward the sequence of self-condensation of allyl alcohol itself, and no understanding of the mechanistic pathway to the (π-allyl)palladium(II) was made. Reported herein is a novel method for synthesizing (π-allyl)palladium complexes from allylic alcohols and cationic palladium(II) complexes (Scheme 1). In addition, a mechanistic aspect of the reaction, where Pd–OH elimination becomes a crucial step, is provided.



Scheme 1.

As given in Table 1, allyl alcohol and mono-substituted allylic alcohols at the 1- or 3-position afford the corresponding π-allyl complexes in good yields (entries 1–5). The reaction is affected strongly by the nature of substituents at the 2-position. For instance, an electron-withdrawing substituent such as R = COOMe results in a good yield of **2f** (entry 6), whereas alkyl groups such as R = Me inhibit the reaction (entry 7). When $PdCl_2$ is used in place of $[PdCl]^+X^-$ in the reaction of **1f**, the yield of **2f** is reduced to 19% (entry 6), while the use of $[PdCl]^+BF_4^-$ in place of $[PdCl]^+OTf^-$ results in virtually no change in the yield (entry 5). A ten-fold excess of substrate per Pd at least is preferable for higher yields of **2** (e.g. entries 5 and 8). The presence of O_2 gives a detrimental effect on this reaction (entry 9).

Allylic alcohol **1h** bearing two Me groups at the C-1 position, when treated with $[PdCl]^+OTf^-$, gave only a trace amount of the corresponding π-allyl complex **2h** (Scheme 2). However, the presence of MeOH (two equivalents) afforded the π-allyl complex **2i** (40%) bearing the OMe group, the formation of which is rational-

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[☆] Dedicated to the memory of Professor Rokuro Okawara who was one of the pioneers in the field of organometallic chemistry in Japan.

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Table 1
Synthesis of (π-allyl)palladium(II) complexes from allylic alcohols[a]

Entry	Allylic alcohols				π-Allyl complexes	
	1	R^1	R^2	R^3	**2**	Yield (%)[b]
1	**a**	H	H	H	**a**	88
2	**b**	Me	H	H	**b**	81
3	**c**	Ph	H	H	**c**	80
4	**d**	H	H	Me	**d**	63
5	**e**	H	H	Ph	**e**	65 (59)[c]
6	**f**	H	COOMe	H	**f**	70 (19)[d]
7	**g**	H	Me	H	**g**	2
8	**e**	H	H	Ph	**e**	49[e]
9	**e**	H	H	Ph	**e**	35[f]

[a] The reaction was performed by using the ratio of **1**/Pd = 10, and the details are given in the text.

[b] Isolated yield.

[c] $[PdCl]^+BF_4^-$ was used in place of $[PdCl]^+OTf$.

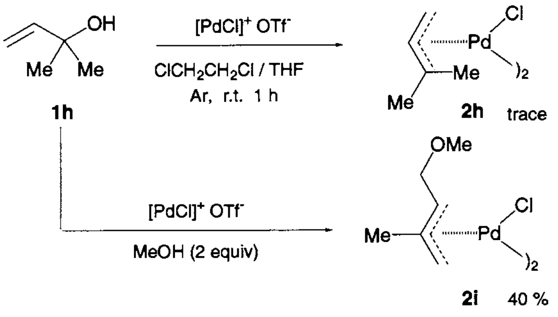
[d] $PdCl_2$ was used in place of $[PdCl]^+OTf$.

[e] The ratio of **1**/Pa was 2.

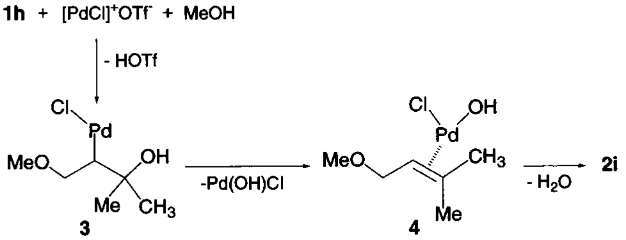
[f] Under O_2.

ized by Scheme 3. Thus, methoxypalladation leading to **3** followed by Pd–OH elimination [5] affords the π-complex **4** of Pd(OH)Cl in which the anionic OH ligand enforces to remove the allylic hydrogen to give **2i** along with H_2O. This view is supported by Beak's observation [6] that the allylic hydrogen is similarly eliminated by anionic Cl ligand of palladium(II).

Based on the process of Scheme 3, the formation of the π-allyl complex **2a** from allyl alcohol **1a** itself can be envisioned as shown in Scheme 4, where the crucial step also lies in the elimination of allylic hydrogen by the OH ligand in complex **6**. The complex **6** must be derived from addition of H–Pd–Cl species to **la** and subsequent Pd(OH)Cl elimination. In this context, how is the H–Pd–C1 species formed? Usually it is expected that the allylic OH group coordinates to Pd(II) to afford RCH_2–O–Pd(II)– from which the Cl–Pd–H species is formed along with aldehyde. However, since none or a trace amount of aldehyde was detected by NMR from the reaction mixture of **1e** or **1f**, the formation of the Pd–H species in Scheme 4 does not meet with this expectation. The reaction of **1a** with $[PdCl]^+OTf^-$ gives **2a** with tetrahydrofuran **8** (Scheme 5) arising from three units assemble of **1a**. Thus, the Pd–H species required for the formation of π-allyl complex **2** must arise from the pathways shown in Scheme 5. Oxypalladation of the allylic OH in **1a** toward the alkene of another molecule **1a** gives **9**. The resulting σ–Pd–C bond in **9** undergoes intramolecular insertion into the C=C bond to give **10**. The tetrahydrofuran **8** is then derived from **10** via Pd–H elimination, isomerization of the olefin in **11**, and addition of another molecule of **1a** to **7**. The resulting H–Pd–C1 species thus leads to the π-allyl complex **2** as shown in Scheme 4 involving Pd–OH elimination hitherto is not well-documented.



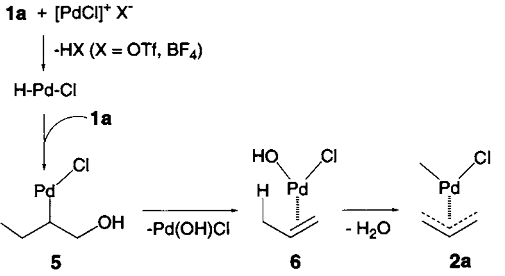
Scheme 2.



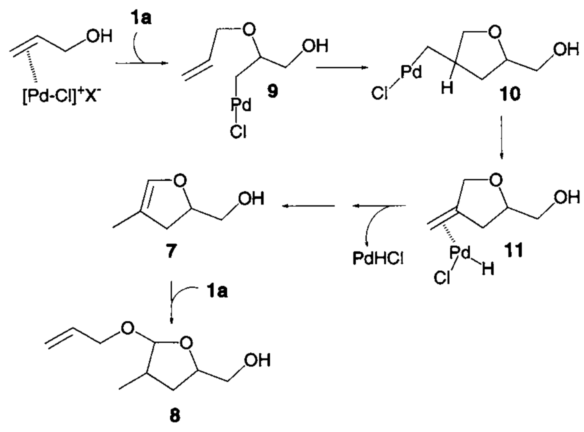
Scheme 3.

In the context mentioned above, one may imagine that the OH elimination from **3** (Scheme 3) or **5** (Scheme 4) could be induced by H^+ formed in situ. However, even if it occurs, the resulting cationic moiety of palladium would not lead to the π-allyl Pd(II) complexes as a result of the oxidation state of palladium. Similarly, elimination of OH from allylic alcohols by either H^+ or cationic Pd(II) does not lead to the π-allyl complexes.

Finally, a typical synthetic procedure for the (π-allyl)palladium complex is given below. In a 100 ml three-necked round-bottom flask equipped with a pressure-equalizing funnel $PdCl_2(MeCN)_2$ (52 mg, 0.20 mmol) was dissolved in 1,2-dichloroethane (40 ml). Allyl alcohol (**1a**) (116 mg, 2.0 mmol) was added to the flask under argon atmosphere. A solution of AgOTf (51



Scheme 4.



Scheme 5.

mg, 0.20 mmol) in THF (5 ml) was added dropwise to the above solution. The mixture was stirred for 1 h at room temperature, and filtered through Florisil. Evaporation followed by the addition of ether to the residue gave a yellow complex of the π-allyl complex **2a** in 88% yield. The compound **8** (R_f 0.325, hexane/EtOAc/$CH_2Cl_2 = 2/1/1$) was isolated from the residue in 34% yield (based on Pd) by SiO_2 column chromatography (0.7 × 10 cm). NMR and GC-Mass shows that the compound **8** consists of four diastereoisomers (1.0/2.0/2.2/2.2), though the structural details are unfortunately unable to be determined.

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