Reaction of palladium(II) complexes with allylsilanes: convenient synthesis of [.eta.3-1-silylallyl]palladium complexes

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Reaction of Palladium(II) Complexes with Allylsilanes: Convenient Synthesis of [η^3-1-(Silyl)allyl]palladium Complexes

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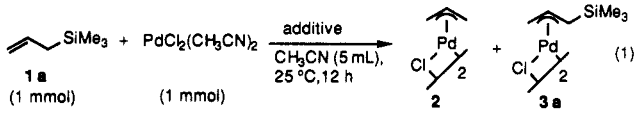
Summary: While the reaction of allyltrimethylsilane with $PdCl_2(CH_3CN)_2$ gave (η^3-allyl)palladium chloride by desilylation, addition of Et_3N changed the reaction course completely, leading to a different product [η^3-1-(trimethylsilyl)allyl]palladium chloride by deprotonation.

The great diversity of the chemistry of η^3-allyl transition metal complexes has been reported. In particular, (η^3-allyl)palladium chemistry has been well investigated, and its application to organic synthesis has been developed and exploited.[1] The early definitive studies of allylpalladium complexes concerned the preparation of dimeric palladium chloride complexes. (η^3-Allyl)palladium derivatives are readily available from alkenes by reactions with Pd(II) complexes like $PdCl_2$, Na_2PdCl_4, and $Pd(OAc)_2$ under appropriate conditions via deprotonation.[2] Analogously, reaction of $PdCl_2(PhCN)_2$ with olefins containing electron-withdrawing β-substitutents, in particular carbonyl, formed (η^3-allyl)palladium complex under mild conditions.[3] If deprotonation occurred in the reaction of allylsilane with Pd(II) salts, [η^3-1-(silyl)allyl]palladium complexes[4] might be obtained. However, the reaction of palladium(II) salt with allylsilane usually affords (η^3-allyl)palladium derivatives by desilylation under mild conditions.[4,5] We wish to report here selective synthesis of [η^3-1-(silyl)allyl]palladium chloride by the reaction of palladium(II) salts with allylsilanes. The new reaction does not involve usual desilylation.

Results and Discussion

The reaction of allyltrimethylsilane (**1a**) with $PdCl_2(CH_3CN)_2$ in CH_3CN at 25 °C afforded anticipated (η^3-allyl)palladium chloride **2** in high yield (91%), an electrophilic reaction of Pd(II) with the double bond assisted by nucleophilic attack of a chloride ion on the silicon atom.[5] Looking for a mild process for deprotonation in this combination, the same reaction was examined in the presence of some additives, amines or Li_2CO_3, and triethylamine was found to be effective for the desired reaction to give [η^3-1-(trimethylsilyl)allyl]palladium chloride[6] **3a** (41% yield) with **2** (7% yield) (eq 1). Note that the labile cationic leaving group, the trimethylsilyl group, was left intact. Addition of Li_2CO_3 led to exclusive formation of **2**. Other amines were not effective; DBU, TMEDA, and pyridine gave insoluble amine complexes, and imidazole gave palladium black. Furthermore, when the method of Ketley and Braatz using $NaHCO_3$ as an additive[7] was applied to this reaction, only small amounts of **2** and **3a** were obtained (12 and 10% yields, respectively).



additive	yield, %[a]	
none	91	–
Et_3N (1 mmol)	7	41
Li_2CO_3 (2 mmol)	33	–

[a] NMR yield based on $PdCl_2(CH_3CN)_2$ used

Table I. Effect of the Amounts of Allylsilane and Et_3N in Eq 1

allylsilane, mmol	Et_3N, mmol	yield,[a] % 2	yield,[a] % 3a[b]
1	1	7	41
	3		40
2	3	2	71
3	1	15	74
	2	6	81
	3		80
5	3		82 (82)[c]

[a] All yields refer to the NMR yield based on the $PdCl_2(CH_3CN)_2$ used. [b] **3a** was obtained as a mixture of syn and anti isomers (uniformly 75/25). [c] Isolated yield.

The effect of the amounts of amine and allylsilane was investigated to optimize the reaction conditions, and the results are summarized in Table I. The use of more than 3 equiv of Et_3N with respect to $PdCl_2(CH_3CN)_2$ was required to suppress the formation of **2**, and the use of

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[7] Ketley, A. D.; Braatz, J. *J. Chem. Soc., Chem. Commun.* **1968**, 169. A suspension of 570 mg (5 mmol) of **1a**, 177 mg (1 mmol) of $PdCl_2$ and 887 mg (8.37 mmol) of $NaHCO_3$ in 2.5 mL of $CHCl_3$ was stirred for 5 h at room temperature. A mixture of **3a** (10%) and **2** (12%) was obtained.

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Table II. Effect of Solvent on the Yield of 3a in Eq 1[a]

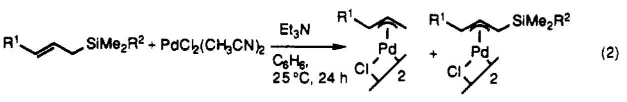
	yield,[b] %	
solvent	**2**	**3a**
CH_3CN		80
THF	5	27
CH_2Cl_2	4	45
C_6H_6		78 (95)[c]
toluene	trace	(78)[c]

[a] Reaction conditions: **1a** (3 mmol), $PdCl_2(CH_3CN)_2$ (1 mmol), Et_3N (3 mmol), solvent (5 mL), 25 °C, 12 h. [b] NMR yield based on $PdCl_2(CH_3CN)_2$ used. [c] 24 h.

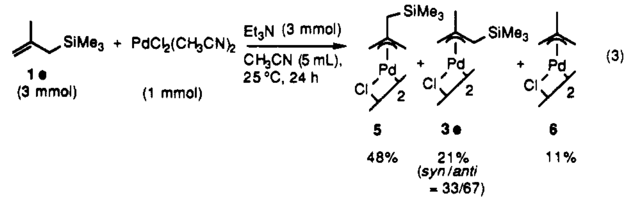
more than 3 equiv of allylsilane was required to afford **3a** in a high yield. Thus, the reaction of 3 equiv of allylsilane with $PdCl_2(CH_3CN)_2$ in the presence of 3 equiv of Et_3N gave **3a** as the sole product (80% yield based on the Pd used).

As can be seen in Table II, the use of THF and CH_2Cl_2 as the solvent led to the formation of the desilylated product **2**. Benzene, CH_3CN, and toluene were solvents of choice for the deprotonation. In particular, the reaction of **1a** with $PdCl_2(CH_3CN)_2$ in benzene at 25 °C gave **3a** exclusively in an excellent yield (95%).

The reaction of other allylsilanes with $PdCl_2(CH_3CN)_2$ was examined (eq 2). Allyldimethylphenylsilane (**1b**) reacted with $PdCl_2(CH_3CN)_2$ to give [η^3-1-(dimethylphenylsilyl)allyl]palladium chloride **3b**[6] in a high yield (84%) with a small amount of **2** (1%). Allyl-*tert*-butyldimethylsilane (**1c**) also reacted with $PdCl_2(CH_3CN)_2$ to afford [η^3-1-(*tert*-butyldimethylsilyl)allyl]palladium chloride **3c** (21% yield) exclusively. However, desilylation occurred in the reaction of cinnamyltrimethylsilane (**1d**) to give [η^3-1-(phenyl)allyl]palladium chloride **4** (18% yield) and no deprotonation product. The reaction of 2-methyl-3-(trimethylsilyl)propene (**1e**) with $PdCl_2(CH_3CN)_2$ afforded a mixture of deprotonation products [η^3-2-methyl-1-(trimethylsilyl)allyl]palladium chloride **3e**[6] (21% yield) and [η^3-2-[(trimethylsilyl)methyl]allyl]palladium chloride **5** (48% yield) and a desilylation product [η^3-2-(methyl)allyl]palladium chloride **6** (11% yield) (eq 3).



1a : R^1 = H, R^2 = Me	**2**	-	**3a** 95% (*syn*/*anti* = 75/25)
1b : R^1 = H, R^2 = Ph	**2**	1 %	**3b** 84% (*syn*/*anti* = 85/15)
1c : R^1 = H, R^2 = t-Bu	**2**	-	**3c** 21% (*syn*/*anti* = 75/25)
1d : R^1 = Ph, R^2 = Me	**4**	18%	**3d** -



A plausible mechanism is described below, but it is only speculative at this time. The desilylation gives (η^3-allyl)palladium chloride.[5] Although not clear, a possible role of Et_3N may be as follows. The reaction may begin with an electrophilic interaction of the Pd(II) with the double bond followed by either nucleophilic desilylation by Cl^- or deprotonation[8] by Et_3N in a competitive manner to afford **2** or **3a**, respectively.

We described here an efficient synthesis of (η^3-allyl)palladium complexes containing a silyl group by the reaction of $PdCl_2(CH_3CN)_2$ with allylsilanes involving deprotonation instead of the usual desilylation. Studies on the reaction of the [η^3-1-(silyl)allyl]palladium complexes thus obtained, in particular complex **5** which might be an interesting precursor to (trimethylenemethane)palladium,[9] are in progress.

Experimental Section

^1H NMR spectra were recorded on a JEOL-GSX-270 (270-MHz) spectrometer as solution in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). Melting points were determined on a Mitamura Riken Kogyo micro melting point apparatus and are uncorrected. The characterization of **3a**, **3b**, and **3e** was described in previous papers.[6]

Reaction of Allyltrimethylsilane (1a) with $PdCl_2(CH_3CN)_2$. Under a nitrogen atmosphere, 259 mg (1 mmol) of $PdCl_2(CH_3CN)_2$ was suspended in 5 mL of dry CH_3CN. Allyltrimethylsilane (**1a**, 114 mg, 1 mmol) was added, and the mixture was stirred at 25 °C for 1 h. The reaction mixture was concentrated, and the product was isolated by column chromatography (Florisil, 15-mm i.d. × 200-mm length, CH_2Cl_2), and the eluent of yellow band was concentrated to give (η^3-allyl)palladium chloride (**2**) (165 mg, 90%).

Reaction of Allyltrimethylsilane with $PdCl_2(CH_3CN)_2$ in the Presence of Triethylamine. Preparation of [η^3-1-(trimethylsilyl)allyl]palladium Chloride (3a). Under an atmosphere of nitrogen, 259 mg (1 mmol) of $PdCl_2(CH_3CN)_2$ and 303 mg (3 mmol) of triethylamine were dissolved in 5 mL of dry CH_3CN. Allyltrimethylsilane (**1a**) (342 mg, 3 mmol) was added and the mixture was stirred at 25 °C for 12 h. The reaction mixture was concentrated and separated by column chromatography (Florisil, 15-mm i.d. × 200-mm length, CH_2Cl_2/hexane = 1/1), and the eluent of the yellow band was concentrated to give [η^3-1-(trimethylsilyl)allyl]palladium chloride (**3a**) (209 mg, 82%).

[η^3-1-(*tert*-Butyldimethylsilyl)allyl]palladium Chloride (3c). The complex **3c** was prepared in benzene from **1c** by the method described above. Yield: 21% (syn/anti = 75/25). Mp: 139–143 °C dec. ^1H NMR ($CDCl_3$): δ (syn) 0.14 (s, 3 H), 0.22 (s, 3 H), 0.91 (s, 9 H), 2.96 (d, J = 11.2 Hz, 1 H), 2.99 (d, J = 13.7 Hz, 1 H), 4.07 (d, J = 6.1 Hz, 1 H), 5.31 (ddd, J = 13.7 Hz, 11.2, 6.1, 1 H); δ (anti) 0.25 (s, 3 H), 0.32 (s, 3 H), 0.86 (s, 9 H), 3.04 (d, J = 12.5 Hz, 1 H), 3.97 (d, J = 9.8 Hz, 1 H), 3.98 (d, J = 7.1 Hz, 1 H), 5.85 (ddd, J = 12.5 Hz, 9.8, 7.1, 1 H). Anal. Calcd for $C_9H_{19}ClPdSi$: C, 36.37; H, 6.44. Found: C, 36.23; H, 6.56.

[η^3-2-[(Trimethylsilyl)methyl])allyl]palladium Chloride (5). A mixture of **5**, **3e**, and **6** was obtained from **1b** by the method described above. Complex **5** was isolated by column chromatography (silica gel 100–200 mesh, CH_2Cl_2/hexane = 1/1, R_f = 0.35) followed by recrystallization from CH_2Cl_2/hexane (1/1). Yield: 16%. Mp: 148–152 dec. ^1H NMR ($CDCl_3$): δ 0.09 (s, 9 H), 1.90 (s, 2 H), 2.74 (s, 2 H), 3.67 (s, 2 H). Anal. Calcd for $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62. Found: C, 30.92; H, 5.83.

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