# A Novel Rearrangement of Chromium Allyloxy(aryl)carbene Complexes Catalyzed by Pd(0)

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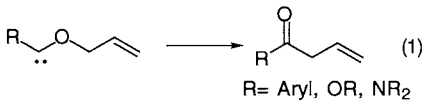
(Received September 25, 1998; CL-980745)

Chromium allyloxy(aryl)carbene complexes undergo formal [2,3]- or [1,2]-sigmatropic rearrangement by the catalytic use of $Pd(PPh_3)_4$ under CO atmosphere. The reaction is considered to proceed *via* palladium aroyl π-allyl complex, which is converted to the corresponding aryl ketones by reductive elimination.

Allyloxycarbenes are known to form allyl ketones by [2,3]-sigmatropic rearrangement.[1,2] Due to the poor availability of the appropriate precursors of these carbenes, few applications for synthetic reactions have been reported except Büchi's allyl amide synthesis.[3-5]




Although pentacarbonylchromium alkoxycarbene complexes sometimes show the reactivity of free alkoxycarbenes such as cyclopropanation reaction,[6] there is no report on the [2,3]-sigmatropic rearrangement of allyloxy[7] nor allylamino[8] carbene chromium complexes, which are converted only to stable metal alkene-carbene complexes.[9,10] Here we would like to describe the first example of formal [2,3]- or [1,2]-sigmatropic rearrangement from chromium allyloxy(aryl)carbene complexes catalyzed by $Pd(PPh_3)_4$ under mild conditions. Very recently, Sierra also reported self-dimerization and C-H insertion reactions of chromium alkoxycarbene complexes catalyzed by $Pd(OAc)_2$.[11]

In the course of our studies on acylchromate complexes,[12] we investigated transformation of chromium alkoxycarbene complexes to acylchromate complexes by removing the alkyl group of the alkoxy group.[12c,13] When a chromium allyloxycarbene complex **1a**[14] was treated with a catalytic amount of $Pd(PPh_3)_4$, the desired deprotection of allyl moiety didn't take place predominantly and a formal [2,3]-sigmatropic rearrangement product **2a** was obtained. That phenomenon prompted us to optimize such a rearrangement reaction. The representative results on the screening of the reaction conditions are summarized in Table 1.

First, the reaction was tried in various kind of solvents (entries 1,2 and 4), and $CH_2Cl_2$ was found to be a suitable one. When the reaction was carried out in CO atmosphere, the yield of the allyl ketone **2a** was increased (entries 3 and 5). Especially in $CH_2Cl_2$ formation of by-products **3a** and **4a** was suppressed effectively and the yield of **2a** was increased to 71%. Among various kinds of palladium catalysts screened (entries 5-9), $Pd(PPh_3)_4$ was found to be most efficient, although many Pd catalysts such as $Pd(OAc)_2$ were also applicable.[15]

As shown in Table 2, not only 4-tolyl complex **1a**, but also 4-$MeOC_6H_4$ and 2-$MeOC_6H_4$ complexes **1b** and **1c** reacted with 1 mol% of $Pd(PPh_3)_4$ smoothly, giving the corresponding ketones **2b** and **2c** in good yields. For the rearrangement of **1d**, having methyl group on the α-position of allyl moiety, 3 mol% of the Pd catalyst was required and the reaction was carried out at room temperature to accomplish the reaction, giving the product **2d** in low yield (29 %).

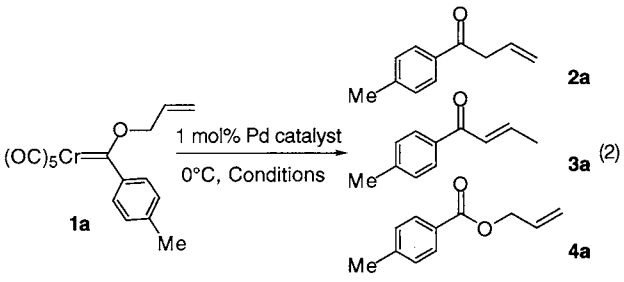



**Table 1.** Reaction conditions of Pd catalyzed reaction of **1a**

| Entry | Catalyst | Solvent | Atm. | Time / h | Yields/ % 2a | 3a | 4a |
|---|---|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | Toluene | Ar | 2 | 0 | 38 | 4 |
| 2 | $Pd(PPh_3)_4$ | THF | Ar | 5 | 19 | 0 | 9 |
| 3[a] | $Pd(PPh_3)_4$ | THF | CO[d] | 2.5 | 35 | 29 | 3 |
| 4 | $Pd(PPh_3)_4$ | $CH_2Cl_2$ | Ar | 6 | 33 | 6 | 17 |
| 5 | $Pd(PPh_3)_4$ | $CH_2Cl_2$ | CO[d] | 17 | 71 | 0 | 4 |
| 6 | $Pd(OAc)_2$ | $CH_2Cl_2$ | CO[d] | 1 | 42 | 0 | 2 |
| 7 | $PdCl_2(PhCN)_2$ | $CH_2Cl_2$ | CO[d] | 1 | 47 | 4 | 4 |
| 8 | $PdCl_2(dppf)$[b] | $CH_2Cl_2$ | CO[d] | 24 | 34 | 0 | 6 |
| 9 | $Pd(dba)_2$[c] | $CH_2Cl_2$ | CO[d] | 1 | 6 | 13 | 0 |

[a]room temperature. [b]dppf: 1,1'-bis(diphenylphosphino)ferrocene. [c]dba: dibenzylideneacetone. [d]1 atm.

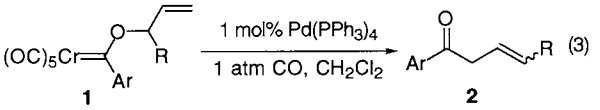



**Table 2.** Pd catalyzed rearrangement of the complex **1**

| Entry | Complex | Ar | R | Temp / °C | Time / h | Yield / % |
|---|---|---|---|---|---|---|
| 1 | **1a** | 4-$MeC_6H_4$ | H | 0 | 17 | 71 (**2a**) |
| 2 | **1b** | 4-$MeOC_6H_4$ | H | 0 | 18 | 92 (**2b**) |
| 3 | **1c** | 2-$MeOC_6H_4$ | H | 0 | 17 | 84 (**2c**)[b] |
| 4[a] | **1d** | 4-$MeC_6H_4$ | Me | 0 to rt | 36 | 29 (**2d**) |

[a]3 mol% of $Pd(PPh_3)_4$ was used. [b]α,β–unsaturated ketone **3c** was also obtained in 16% yield.

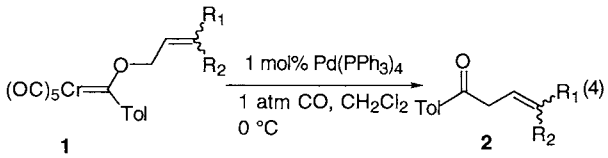
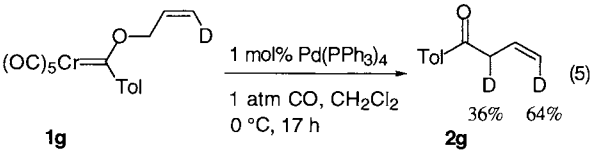



**Table 3.** Pd catalyzed rearrangement of the complex **1**

| Entry | Complex | $R_1$, $R_2$ | Time / h | Yield / % |
|---|---|---|---|---|
| 1 | **1e** | Me, H[a] | 34 | 51 (**2e**)[b] |
| 2 | **1f** | Me, Me | 27 | 32 (**2f**) |

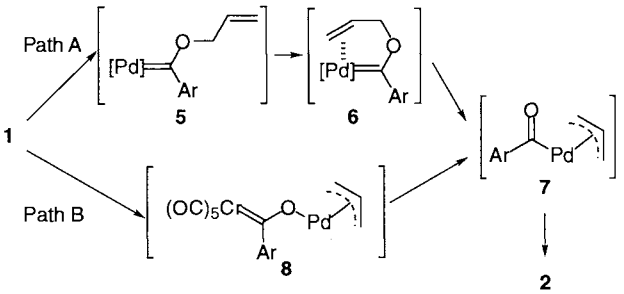
[a]*cis* : *trans* = 1 : 2. [b]*cis* : *trans* = 1 : 4.

As shown in Table 3, from crotyl cómplex **1e** and prenyl complex **1f**, formal [1,2]-sigmatropic rearrangement product **2e** and **2f** were obtained, respectively. In order to assign which type of rearrangement proceeded in the case of non-substituted allyloxy complexes, D-substituted complex **1g** was treated with the Pd catalyst to give the product **2g**, in which D was distributed both at α and γ position (eq. 5).




Two reaction pathways are considered (Scheme 1). As being proposed by Sierra *et al*,[11] transmetallation might occur to generate a palladium carbene complex **5** (path A). After the formation of the palladium alkene-carbene complex **6**, aroyl allyl palladium complex **7** is produced, which is converted to the product **2** by reductive elimination.

The other mechanism is shown in path B. A π-allyl palladium complex is initially produced to give acylchromate complex **8**. In the presence of CO, the complex **8** is converted to the aroyl intermediate **7** to eliminate the product **2**.




**Scheme 1.** Plausible mechanisms.

As described above, we found that the formal [2,3]- or [1,2]-sigmatropic rearrangement occurs from chromium allyloxycarbene complexes catalyzed by Pd(0) under very mild conditions. The reaction is considered to proceed *via* palladium aroyl π-allyl complexes. Thus, the combination of group 6 metal carbene complexes and late transition metal complexes would provide unique reactions.

## References and Notes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15 General procedure. The chromium complex **1** (0.1 mmol) and $Pd(PPh_3)_4$ (1.3 mg, 0.001 mmol) are placed into a Schlenk flask and the flask is connected to a vacuum line. After the flask is chilled by $CO_2$-acetone bath, 4 mL of $CH_2Cl_2$ (dried over $CaH_2$) is vacuum transferred into the flask and the flask is filled with CO (1 atm). After being stirred at 0 °C for several hours listed in Tables, the solution is passed through Celite pad and the solvent is evaporated. The product **2** is obtained by silica gel chromatography.