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

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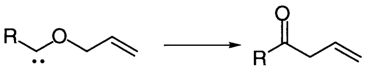
Chromium allyloxy(aryl)carbene complexes undergo formal [2,3]- or [1,2]-sigmatropic rearrangement by the catalytic use of $Pd(PPh_3)_4$ under CO atmosphere. The reaction is considered to proceed *via* palladium aroyl π-allyl complex, which is converted to the corresponding aryl ketones by reductive elimination.

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]



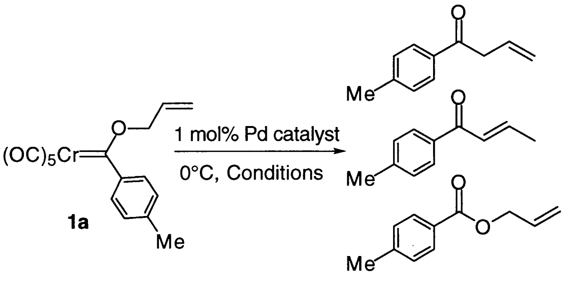
(1)

R= Aryl, OR, NR_2

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]

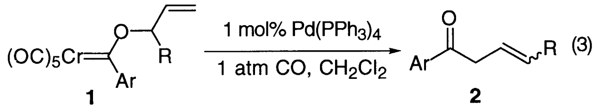


1a **2a** **3a** **4a** (2)

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.



1 **2** (3)

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

Entry	Complex	Ar	R	Temp / °C	Time / h	Yield / %
1	**1a**	$4\text{-}MeC_6H_4$	H	0	17	71 (**2a**)
2	**1b**	$4\text{-}MeOC_6H_4$	H	0	18	92(**2b**)
3	**1c**	$2\text{-}MeOC_6H_4$	H	0	17	84(**2c**)[b]
4[a]	**1d**	$4\text{-}MeC_6H_4$	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.

As shown in Table 2, not only 4-tolyl complex **1a**, but also $4\text{-}MeOC_6H_4$ and $2\text{-}MeOC_6H_4$ 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 %).

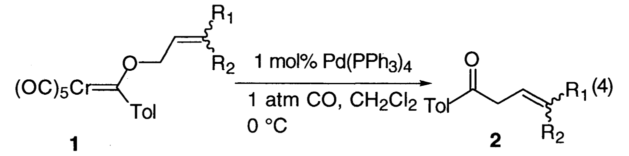
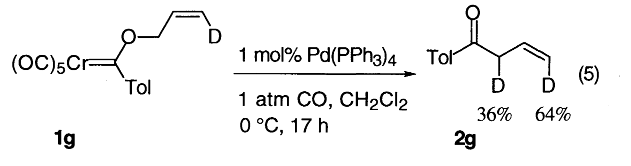


Table 3. Pd catalyzed rearrangement of the complex **1**

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**)

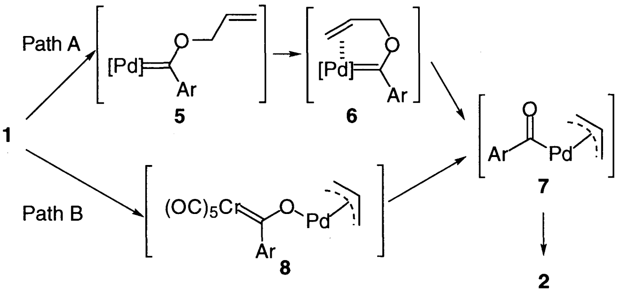
[a] *cis* : *trans* = 1 : 2. [b] *cis* : *trans* = 1 : 4.

As shown in Table 3, from crotyl cômplex **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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