Palladium Catalyzed Coupling Reaction of Acylchromate Complexes and Allylic Bromides

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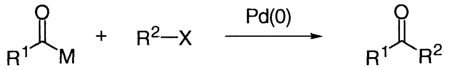
A cross-coupling reaction between acylchromate complexes and allylic bromides takes place under CO atmosphere in the presence of a catalytic amount of $Pd(PPh_3)_4$ to afford the corresponding allylic ketones in good yield. The same reaction also proceeds by adding RNC under argon atmosphere in place of CO atmosphere. Thus, the acylchromate complex works as a good acyl donor for Pd catalyzed acylation reaction.

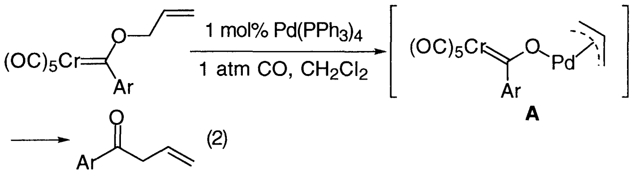
A transition-metal catalyzed cross-coupling reaction of alkyl halide and acylmetal has been considered as a promissing method for the unsymmetrical ketone synthesis. Several examples using acyltin as an acylmetal component have been reported,[1] however, these reactions have found a limited application for the practical synthesis of ketones partly due to the unavailability and instability of the starting acyltin compounds.



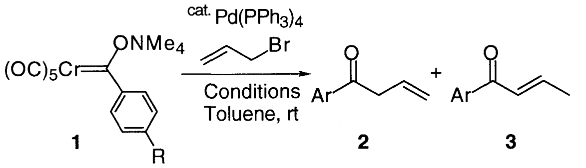
(1)

Some of the transition-metal acyl complexes such as iron,[2] nickel,[3] and cobalt[4] complexes show the reactivity of acyl anion equivalents, whereas their utilization toward the acyl donor for transition metal catalyzed cross-coupling reaction has not been reported.[5,6] Here we wish to report the palladium catalyzed cross-coupling reaction of allylic bromides by using acylchromate complexes as acylmetal components.

Previously we reported a novel rearrangement from allyloxy(aryl)chromium carbene complexes to allyl aryl ketones catalyzed by $Pd(PPh_3)_4$ (eq. 2).[7] A plausible intermediate of this reaction is a bimetallic complex **A**, which suggested us to investigate the cross-coupling reaction between allylic halides and acylchromate complexes.



The reaction of aroylchromate complex **1**[8] with allyl bromide in the presence of $Pd(PPh_3)_4$ was examined. The results are shown in Table 1. Firstly, tetramethylammonium salt of 4-methoxybenzoylchromate complex **1a** was treated with 5 molar amounts of allyl bromide in the presence of 10 mol% of $Pd(PPh_3)_4$ under 1 atm CO to give the desired allyl ketone **2a** in 83% yield (entry 1). Interestingly, the yield was increased by reducing the amount of the Pd catalyst (entries 1-3), e.g. the use of 2 mol% of the Pd afforded **2a** quantitatively (entry 3). In the absence of the Pd catalyst, the reaction did not take place (entry 4). As shown in entry 5, though this coupling reaction also occurred under argon atmosphere, the yield was apparently low and the conjugate ketone **3a** was obtained as a side product. The amount of allyl bromide can also be reduced to be almost stoichiometric (entry 6). Finally, substituent effect was observed under the conditions of 1 mol% $Pd(PPh_3)_4$ and 1.4 molar amounts of allyl bromide (entries 6-8).[9] All of the substrates (**1a**-**1c**) gave satisfactory results but it was observed that the yield was slightly diminished when an electron withdrawing group such as CF_3 group was introduced on the phenyl group.

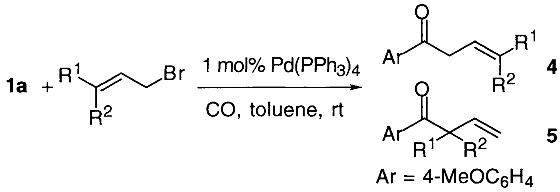


(3)

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

Entry	R	Equiv. of C_3H_5Br	Pd / mol%	Atm.	Time / h	Yields/ % **2**	**3**
1	OMe(**1a**)	5.0	10	CO	19	83	0
2	OMe	5.0	5	CO	19	90	0
3	OMe	5.0	2	CO	19	99	0
4	OMe	3.0	0	CO	32	0	0
5	OMe	5.0	2	Ar	24	66	13
6	OMe	1.4	1	CO	18	92	0
7	H(**1b**)	1.4	1	CO	18	90	0
8	CF_3(**1c**)	1.4	1	CO	19	84	0

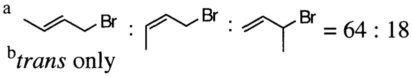
Next, substituted allylic bromides were employed. The results are shown in Table 2. Although longer reaction time was required to complete the reactions, the total yield of the products was still high.



(4)

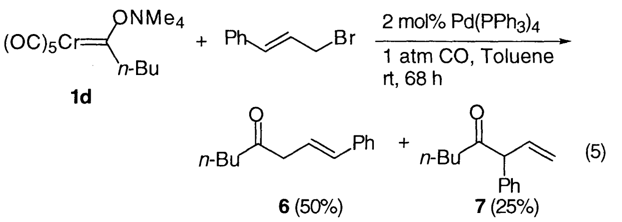
Table 2. Reaction with substituted allylic bromides

R^1	R^2	Time / h	Yields/ % **4**	**5**	total
Me	Me	18	42	15	57
Me	Me	39	43	41	84
Ph	H	43	69[b]	27	96
Me[a]	H[a]	43	39[b]	54	93

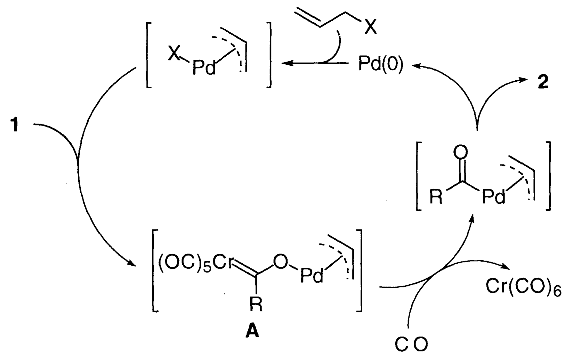
[a]  = 64 : 18 : 18

[b] *trans* only

Not only aroylchromate complexes but also alkanoylchromate can be used. When butanoylchromate complex **1d** was treated with cinnamyl bromide in the presence of the Pd catalyst, the cross-coupling products **6** and **7** were obtained in 50% and 25% yield, respectively (eq. 5).

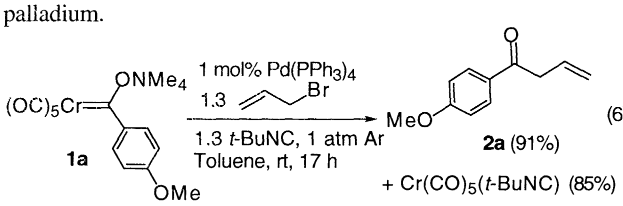


The mechanism of this reaction is considered as shown in Scheme 1. The reaction between π-allyl palladium complex and acylchromate complex **1** would give the bimetallic complex **A**.[10] CO might attack on chromium, causing the cleavage into $Cr(CO)_6$ and acyl π-allyl palladium complex, which gives the product **2** with regeneration of Pd(0).

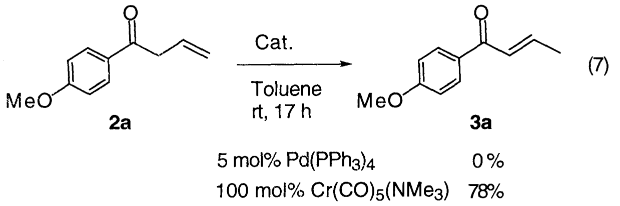


Scheme 1. Plausible mechanism.

The effect of CO seems to be very important. CO mainly plays a role to produce coordinatively saturated $Cr(CO)_6$. Two positions are considerable where CO attacks, on chromium or on palladium. When *t*-BuNC was used under argon atmosphere in place of CO, the ketone **2a** was obtained in 91% yield accompanied with $Cr(CO)_5$(*t*-BuNC) in 85% yield (eq. 6). No formation of the corresponding imine 4-$MeOC_6H_4C$(=N-*t*-Bu)$CH_2CH{=}CH_2$ was observed, which strongly suggested that CO and *t*-BuNC might attack directly on chromium, not on palladium.



Furthermore, isomerization from **2** to **3** is also suppressed under CO atmosphere. In the absence of CO or RNC, coordinatively unsaturated chromium complex $Cr(CO)_5$(solvent) is generated, and induces such an isomerization. That is, when **2a** was treated with $Cr(CO)_5(NMe_3)$[11], a substitute for $Cr(CO)_5$(solvent), in toluene at room temperature for 17 h, isomerized ketone **3a** was obtained in 78% yield, while no isomerization was observed when only $Pd(PPh_3)_4$ was present (eq. 7).



As described above, acylchromate is found to be an excellent acyl donor for Pd(0) catalyzed cross-coupling reaction. The reaction proceeds efficiently in the presence of CO or RNC, and $Cr(CO)_5L$ can also be recovered under the reaction conditions.[12] Though the acylchromate complex is known to show the reactivity as an acyl anion, only the 1,4-addition reaction to electron-deficient olefin is realized.[13] The treatment with other metallic reagent can change the reactivity of the acylchromate complex,[14] which may enlarge the applicability of the complex toward the organic synthesis.

References and Notes

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5 Hegedus and Tamura reported the stoichiometric reaction of acyliron and acylnickel complexes with π-allyl palladium complex, giving the corresponding allyl ketones. See, L. S. Hegedus and R. Tamura, *Organometallics*, **1**, 1188 (1982).

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9 General procedure. A mixture of the chromium complex **1** (0.1 mmol), allyl bromide (0.14 mmol), and $Pd(PPh_3)_4$ (0.001 mmol) in toluene (5 mL) is stirred at room temperature for several hours listed in Tables. After the reaction mixture is diluted with Et_2O, the solution is passed through Celite pad and the solvent is evaporated. The product **2** is obtained by silica gel chromatography.

10 The structure of the bimetallic complex **A** is still speculative.

11 J. M. Maher, R. P. Beatty, and N. J. Cooper, *Organometallics*, **4**, 1354 (1985).

12 It is practically difficult to recover $Cr(CO)_6$ effectively, which easily sublimes, especially in small scale. From the viewpoint of easiness for the recovery, it is more convenient to perform the reaction under isocyanide conditions.

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