

Communication

Branch selective allylation of acetylacetone catalyzed by Water-soluble rhodium complex catalyst

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ABSTRACT

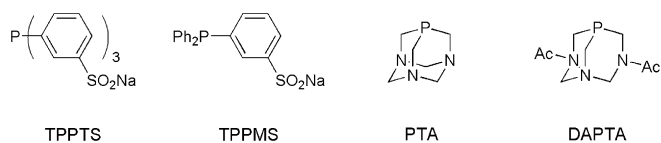
[RhCl(1,5-cod)]₂/PTA is highly active branch-selective catalyst for C-allylation of acetylacetone by allylic carbonates in water/ethyl acetate biphasic system, where either crotyl or 1-methylallyl carbonates gives sterically congested branched allylation product, suggesting formation of a common allylrhodium intermediate.

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1. Introduction

Biphasic catalysis using water/organic solvent attracts significant attentions, since such processes benefits us more green chemical transformation [1]. For example, if the catalyst can stay in water phase, the hydrophobic organic products are easily separated by simple decantation, providing highly cost saving chemical processes due to easy recovery and reuse of the catalyst. Such processes also save the amount of harmful organic solvent in synthesis. We recently reported highly branch-selective allylation of benzenethiols using allylic alcohol catalyzed by water-soluble palladium catalyst (Pd(OAc)₂/TPPTS) using water/hexane biphasic system, where very unusual effect of interface area is also observed [2]. Although sulfonated phosphine ligands such as TPPTS and TPPMS are frequently used as water-soluble ligands in such catalyses, their ionic property might interfere their activity and reactivity [3]. Non-ionic water-soluble phosphorus ligands such as PTA [4] and DAPTA [5], which also have high solubility in water without ionic property, are also considered as one of the promising ligands for providing water-soluble transition metal catalysts. We extended this Pd-catalyzed water/organic solvent biphasic allylation system to Rh catalyst [6]. The high branch-selective C-allylation reaction by a Rh catalyst using branch allylic carbonate in organic solvent has been already reported by J. Tsuji et al. [6a]. On the other hand,

we found that [RhCl(1,5-cod)]₂/PTA is highly active branch-selective water/AcOEt biphasic catalyst for C-allylation of acetylacetone by both of branch and linear allylic carbonates. In this system, allylic acetates can also be used for allylation even without stoichiometric amount of base.



2. Experimental

2.1. Materials

All manipulations were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Water was purified by ion-exchange column followed by distillation, and other solvents were dried over and distilled from appropriate drying agents under N₂ and were stored under nitrogen before use. Ethyl acetate were dried over and distilled from CaCl₂ under N₂. Crotyl, 1-methylallyl, prenyl, and cinnamyl carbonate by the reaction of corresponding allylic alcohol with methyl chloroformate [7]. [RhCl(1,5-cod)]₂ [8], PTA [9], DAPTA [5] and THMP [10] were prepared according to the literature methods. All other chemicals were obtained from commercial sources and used directly without further purification.

Abbreviations: TPPTS, trisodium 3,3',3''-phosphinidynetris(benzenesulfonate); PTA, 1,3,5-triaza-7-phosphaadamantane; DAPTA, 3,7-diacetyl-1,3,7-trisaza-5-phosphabicyclo[3.3.1]nonane; TPPMS, sodium diphenylphosphinobenzene-3-sulfonate.

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2.2. Instrumentation

GC analysis was performed on a Shimadzu GC-14B using a GL Science 30 m × 0.25 mm TC-WAX capillary column.

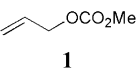
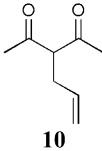
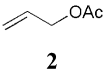
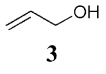
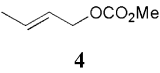
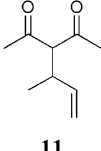
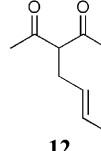
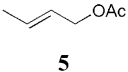
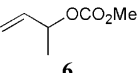
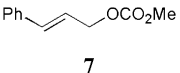
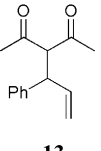
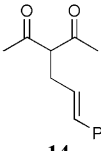
2.3. Catalytic allylation

Typical procedure for catalytic allylation is shown as follows. In a 25-mL Schlenk tube, $[\text{RhCl}(\text{1,5-cod})_2]$ (12.5 mg, 0.025 mmol) and PTA (24.3 mg, 0.155 mmol) were placed under nitrogen atmosphere. Degassed pure water (2.0 mL) was introduced, and the mixture was stirred vigorously for several minutes, then the aqueous solution became a clear yellow solution. AcOEt (2.0 mL), allylic carbonate (68.9 mg, 0.529 mmol) and acetylacetone (50.0 mg, 0.499 mmol) were added to the solution. Biphenyl (15.3 mg, 0.0992 mmol) was added as an internal standard to the solution. After reaction the organic layer was quantitatively analyzed by GLC. All the prepared compounds are known and compared with authentic samples.

3. Results and discussion

Table 1 shows the results of catalytic allylation promoted by water-soluble Rh complex in biphasic system under various conditions. Treatment of allyl methyl carbonate (**1**) with acetylacetone in the presence of 2 mol% $[\text{RhCl}(\text{1,5-cod})_2]$ with 6 equivalents of PTA at room temperature for 3.5 h under nitrogen atmosphere in water/ethyl acetate biphasic media smoothly gave an allylated product (**10**) quantitatively (Entry 1). Other allylating reagents such as allyl acetate (**2**) can also be used with less activity (Entry 2). Unfortunately, allyl alcohol (**3**) could not be used in this reaction (Entry 3), the result being in sharp contrast to Pd/TPPTS system [2]. In these reactions, simple separation of allylated products from catalyst was easily achieved by decantation and the catalyst can be reused with some catalytic activity loss. Both crotyl- (**4**) and 1-methylallyl carbonates (**6**) also gave corresponding allylated products (**11,12**) in high yields at 40 °C (Entries 4,6). One interesting point is that both reactions gave high branch selectivity (98%), suggesting involvement of the common intermediate in

Table 1
Allylation of Acetylacetone Catalyzed by Water-soluble Rhodium Complex Catalyst.^a

Entry	Substrate	Time	Product (ratio)	Total yield%
1 ^b	 1	3.5	 10	97
2	 2	24	10	71
3 ^b	 3	11	10	0
4	 4	3	 11	94
			 12	
			(98/2)	
5	 5	24	11, 12 (98/2)	84
6	 6	48	11, 12 (98/2)	89
7	 7	74	 13	64
			 14	
			(98/2)	

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