Hydrosilylation of Allenes over Palladium-Gold Alloy Catalyst

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Abstract: An efficient synthetic route to alkenylsilnaes involving hydrosilylation of allenes by supported palladium-gold alloy catalysts has been developed. The catalytic activity and the product selectivity were drastically changed by the incorporation of palladium atoms into gold nanoparticles (NPs). The supported Pd-Au alloy catalysts with a low Pd/Au ratio were highly effective for the hydrosilylation at ambient temperature, in which the corresponding β-vinylsilanes were obtained in good to high yields with high selectivity.

Keywords: alloy catalysts, hydrosilylation, allene, vinylsilane.

1. Introduction

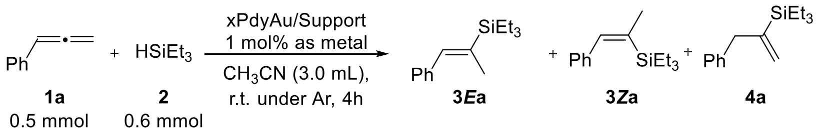
Hydrosilylation of unsaturated organic molecules is the most straightforward and convenient method for the synthesis of organosilicon compounds. A series of monometallic NPs have been used as efficient hydrosilylation catalyst. However, the reactions have often been carried out at elevated temperature because they show lower activities than those of homogenous catalyst. Thus, the development of a novel catalytic system that can operate at ambient temperature would be very important with regard to both synthetic and green chemistry. We recently reported that supported Pd-Au alloy catalyst was effective for hydrosilylation of α,β-unsaturated ketones and internal alkynes under mild reaction conditions[1]. In this study, we found that hydrosilylation of allenes by supported PdAu alloy catalysts gave the corresponding β-vinylsilane as main products, whereas supported Au catalyst mainly furnished the corresponding α-vinylsilane.

2. Experimental

Supported Pd−Au alloy catalysts were prepared through a colloid immobilization method. To an aqueous solution containing the desired molar ratio of $PdCl_2$ to $HAuCl_4$ was added polyvinylpyrrolidone, and the solution was cooled to 273 K. Subsequently, aqueous solution of $NaBH_4$ was added rapidly. After 0.5 h of colloid generation, inorganic support was added to the colloidal solution, which was acidified to pH 1−3 with 0.1 M hydrochloric acid. After vigorous stirring overnight at room temperature, the resulting gray powder was separated from the suspension by centrifugation, and dried overnight at 80 °C. The obtained catalysts were denoted xPd−yAu/support, where x and y denote the molar ratio of Pd to Au. The total loading amount of metal was set at 1 wt %.

3. Results and discussion

The reaction of phenylallene (**1a**) with triethylsilane (**2**) in CH_3CN by the catalyst with different Pd/Au ratio was investigated (Scheme 1). As previously demonstrated by Stratakis et al.[2], the reaction at elevated temperature of 65 °C by Au/TiO_2 catalyst smoothly proceeded to give the corresponding terminal alkenylsilane (**4a**) as a main product with high selectivity (Table 1, entry 1). However, only a trace amount of products was obtained by the reaction with Au/TiO_2 at room temperature (entry 2). In contrast, $1Pd5Au/TiO_2$ showed high



Scheme 1. Hydrosilylation of allenes catalyzed by PdAu alloy catalyst

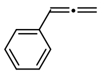
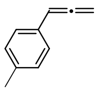
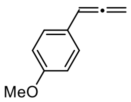
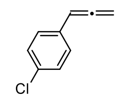
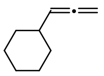
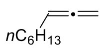
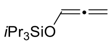
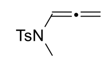
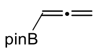
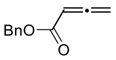
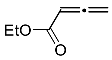
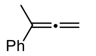
activity even under an ambient condition to afford alkenylsilanes in total yields of 58% and the main product in the reaction turned out to be the internal alkenylsilane with *E* configuration (**3a*E***) (entry 4). No reaction took place in the presence of Pd/TiO_2 catalyst under the present condition (entry 8). The Pd-Au catalysts with a low Pd/Au ratio showed high activity for the present catalytic reactions, and the reaction by 1Pd5Au alloy catalyst furnished the highest total yield of the products (entry 4), whereas the reaction by Pd-Au catalysts with a high Pd/Au ratio resulted in very low yields of the products (entries 6 and 7). The survey of optimal supports for the 1Pd5Au alloy revealed that Al_2O_3-supported Pd-Au catalysts gave the highest yield of the silylated adducts (entry 9).

Table 1. Hydrosilylation of allenes by supported PdAu alloy catalyst

Entry	Catalyst	Yield(%)[a]	Selec. (**3*E*a/3*Z*a/4a**)(%)[a]
1	Au/TiO_2[b]	85	7/0/93
2	Au/TiO_2	4	6/0/94
3	1Pd10Au/TiO_2	7	79/6/15
4	1Pd5Au/TiO_2	58	62/9/29
5	1Pd3Au/TiO_2	53	61/8/31
6	1Pd1Au/TiO_2	3	68/8/24
7	3Pd1Au/TiO_2	0	-
8	Pd/TiO_2	0	-
9	1Pd5Au/Al_2O_3	73	57/8/35

[a]Determined by GC [b]65 °C, 3 h

Table 2. Substrate scope of allenes[a]

			
1a	**1b**	**1c**	**1d**
73% [b]	79%	61%	50%
57/8/35	51/6/43	60/8/32	62/4/34
			
1e	**1f**	**1g**	**1h**
62%	71%	67%[b]	70%
33/0/67	38/2/60	56/0/44	56/0/44
			
1i	**1j**	**1k**	**1l**
60%	58%	55%	34%[b]
75/0/25	81/0/19	80/0/20	59/13/28

[a] Reaction conditions: **1** (0.50 mmol), **2a** (0.60 mmol), 1Pd5Au/Al_2O_3 (1.0 mol% as metal), CH_3CN (3 mL), at r.t.. Isolated yield. Selectivity of the product were determined by ^1H-NMR analysis. [b] Determined by GC.

Under the optimized reaction conditions, the reaction of variety of allenes with triethylsilane was investigated (Table 2). The reaction of allenes with aromatic substituent gave the corresponding alkenylsilanes in good to high yields. In those cases, internal alkenylsilanes with *E*-configuration were obtained as main products (**1a-1d**). Alkyl-substituted allenes also participated as good substrates in the present catalytic system to afford the silylated adducts in satisfactory yields, whereas decreased selectivities of internal alkenylsilane were observed (**1e** and **1f**). Tri-substituted internal alkenes bearing two different heteroatoms could be synthesized by the reaction of *O*- or *N*-atom substituted allenes in high yields (**1g** and **1h**). In the reaction of ester-substituted allenes, increased selectivities for internal silylalkenes were observed without significant decreases in total yields of the product (**1i-1k**). Tri-substituted alkenylsilanes can be prepared by hydrosilylation of internal alkynes, while this protocol never achieves the synthesis of tetra-substituted alkenes bearing silyl groups. Despite the unsatisfactory yield and selectivity of the product, hydrosilylation of 1,1-substituted allene with the present PdAu alloy catalytic system provides the novel route to tetra-substituted silylalkene (**1l**). The high evironmetal compatibility of the present catalysts is reflected in their reusablity. Significant decreases in the yield of the product were not observed during three consecutive catalytic reactions with 1Pd5Au/Al_2O_3.

4. Conclusion

Hydrosilylation of allenes over supported PdAu alloy catalysts was demonstrated. The incorporation of Pd atoms into Au NPs not only drastically enhanced activity of the catalysts but also dramatically changed the product selectivity. The reaction over PdAu alloy at r.t. efficiently proceeded to give the corresponding alkenylsilanes. A wide range of substituted allenes with hydrosilanes were applicable to give the corresponding silylalkenes in good to high yields.

References

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