[2+2+2] cycloaddition of alkynes over supported Pd–Au alloy catalysts

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Abstract: [2+2+2] cycloaddition of alkynes took place effectively over supported Pd–Au alloy catalysts. A variety of alkynes participated in the present heterogeneous catalytic system to give the corresponding polysubstituted arenes in high yields. The reactions took place even under open-air condition, and no decreases in the products yield were confirmed during repeated uses of the supported Pd–Au alloy catalysts.
Keywords: Alloy catalyst, Cycloaddition, Alkyne, Substituted arene.

1. Introduction

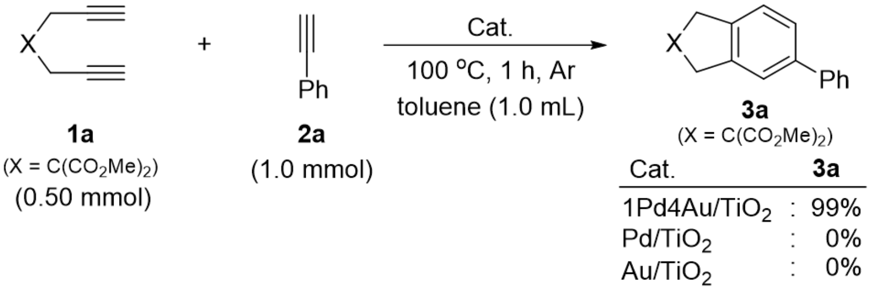
Transition-metal-catalyzed [2+2+2] cycloaddition of alkynes is the most elegant, versatile and atom-economical method to give polysubstituted arenes which are widely used in material, medical and pharmaceutical chemistry. Although various homogeneous catalysts based on transition-metal complexes have been reported to be effective for [2+2+2] cycloaddition of alkynes, heterogeneous variant that can provide environmental benefits is limited to only one example of supported Au catalysts.[1] In addition, the Au catalysis faces with severe limitation of the scope of alkyne substrates. In this study, we found that supported PdAu alloy catalysts were effective for [2+2+2] cycloaddition of various kind of alkynes to provide substituted benzenes in good to high yields.

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 $HAuCl_4 \cdot 3H_2O$ was added poly(*N*-vinylpyrrolidone). Subsequently, aqueous solution of $NaBH_4$ was added rapidly under vigorous stirring. After colloid generation, inorganic support was added to the colloidal solution. After vigorous stirring overnight at room temperature, the resulting gray powder was separated from the suspension by centrifugation, thoroughly washed with distilled water, and dried overnight. The obtained catalysts were denoted xPdyAu/support, where x and y denote the molar ratio of Pd to Au.

3. Results and discussion

The reaction of malonate-derived 1,6-heptadiyne (**1a**) with phenylacetylene (**2a**) was carried out in the presence of TiO_2-supported catalysts (Scheme 1). The reactions by supported monometallic Pd and Au catalysts gave no product. In sharp contrast, alloying Pd and Au allowed to proceed the reaction to give the corresponding biaryl **3a**. Pd–Au alloy NPs with low Pd concentration showed high catalytic activity, and the reaction by 1Pd4Au/TiO_2 gave the product **3a** in a quantitative yield. It is noteworthy that the supported 1Pd4Au/TiO_2 catalyst exhibited high air-



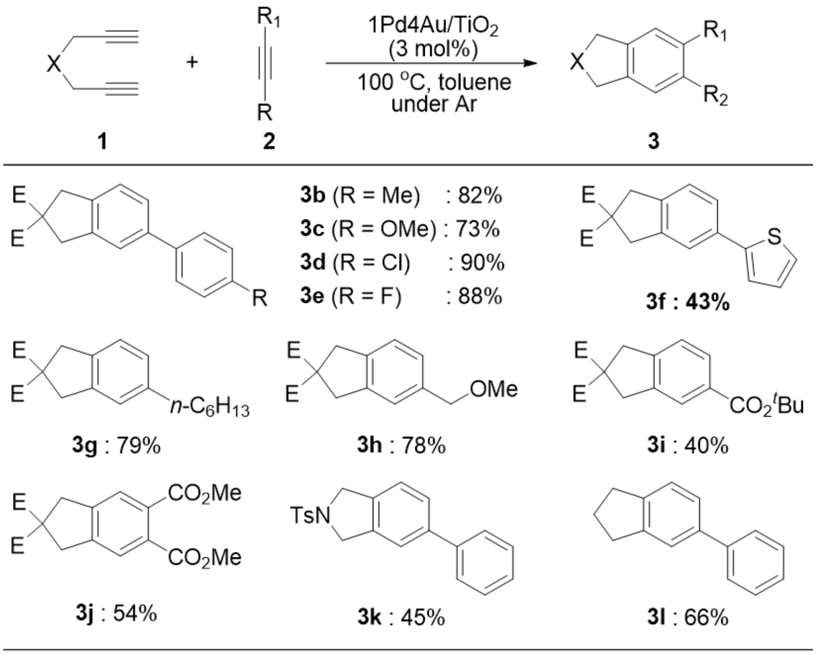
Cat.	3a
1Pd4Au/TiO_2	99%
Pd/TiO_2	0%
Au/TiO_2	0%

Scheme 1. Cross-cycloaddition of diyne (**1a**) and monoyne (**2a**)

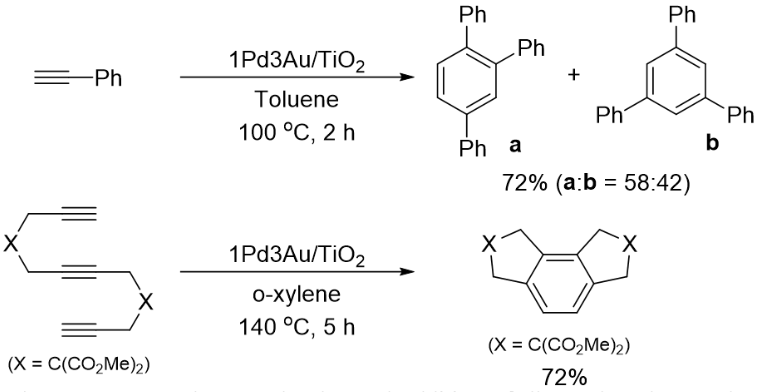
tolerance, and no significant decrease in the yield of the product was observed in the reaction under an open-air condition. Furthermore, Pd–Au alloy catalysts showed excellent reusability, and four consecutive catalytic tests provided the biaryl **3a** in excellent yields, respectively.

With the optimized catalysts in hand, the scope of substrate in the cross cycloaddition of diynes with monoynes was surveyed. A variety of aryl monoynes bearing electron-donating or withdrawing substituents could be used under the Pd–Au NPs catalysis to give the corresponding biaryls in high yields. Thienyl arenes were also accessible. Alkyl acetylenes could participate the Pd–Au NPs catalyzed reactions to give the corresponding arenes in high yields. The reaction of internal alkynes also proceeded to furnish the corresponding arenes in good yields. Additionally, the reaction of a variety of diynes proceeded to give the corresponding arenes in high yields, respectively.

Table 1. Scope of substrates in PdAu-catalyzed cross-cycloaddition



The supported Pd–Au alloy catalysts were effective for different types of alkyne cycloaddition (Scheme 2). Efficient intermolecular cyclotrimerization of alkynes were achieved by the supported Pd–Au alloy catalyst to give the corresponding trisubstituted arenes. Intramolecular cycloaddition of triynes also took place by the use of supported Pd–Au alloy catalysts to form tricyclic compounds.



Scheme 2. Inter- and Intramolecular cycloaddition of alkynes by PdAu catalysts

4. Conclusions

We developed supported Pd-Au alloy catalysts effective for [2+2+2] cycloaddition of alkynes. Various types of alkyne trimerization including inter- or intramolecular and cross-cycloaddition were realized by the use of supported Pd–Au alloy NPs with low Pd/Au molar ratios. A wide range of alkynes could participate the present Pd–Au alloy catalytic systems to give the polysubstituted arenes in good to high yield. The reactions took place even under open-air condition, and no decreases in the products yield were confirmed during repeated uses of the supported catalysts. These intriguing features would be useful in the practical syntheses of highly substituted aromatics.

References

1. A. Leyva-Pérez, J. Oliver-Meseguer, J. R. Cabrero-Antonino, P. Rubio-Marqués, P. Serna, S. I. Al-Resayes, A. Corma, ACS Catal. 3 (2013) 1865.