K_2PtCl_4/AgOTf as a Highly Active Catalyst for Hydroarylation of Propiolic Acids with Arenes

Juzo Oyamada and Tsugio Kitamura*

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University,
Honjo-machi, Saga 840-8502

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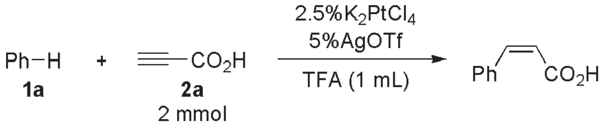
A new and efficient K_2PtCl_4/AgOTf catalyst for the hydroarylation of propiolic acid was found. The hydroarylation of propiolic acids gave predominantly (*Z*)-cinnamic acid derivatives in high yields. The K_2PtCl_4/AgOTf catalyst showed a high activity to less reactive benzene.

The catalytic activation of unreactive C–H bond followed by functionalization such as C–C bond formation is an important reaction for the synthesis of useful chemicals and noticed as an environmentally benign and atom-economy process.[1] For example, it can convert simple, unreactive, and cheap arenes to aryl-substituted compounds directly, without pre-functionalization like halogenation. Hydroarylation of alkynes via aromatic C–H bond activation is one of the most atom-economic reactions and has been studied widely by using various transition-metal catalysts.[2–11]

We reported that the $Pd(OAc)_2$ catalyzed hydroarylation of alkynes proceeded efficiently at room temperature to give aryl-substituted alkenes.[3c,4a] However, the activity of Pd catalyst for less reactive arenes such as benzene and *p*-xylene was low. Moreover, the low selectivity was observed in the Pd-catalyzed hydroarylation of ethyl propiolate. The reaction gave butadiene derivatives along with the usual expected adduct, cinnamates. Very recently, we reported that $PtCl_2$/AgOTf catalyst was selective and effective for the hydroarylation of ethyl propiolate.[4b] The reaction of ethyl propiolate gave the corresponding cinnamate selectively, without butadiene derivatives.[4b] However, the $PtCl_2$ catalyst exhibited a low activity toward less reactive aromatics and could not be applied to the hydroarylation with a representative aromatic compound, benzene. In our continuous study on Pt-catalyzed hydroarylation, we found that K_2PtCl_4 was a more active pre-catalyst than $PtCl_2$. Here, we report the effective hydroarylation of propiolic acids with the aid of a new and efficient catalyst, K_2PtCl_4/AgOTf.

K_2PtCl_4 is one of the most readily available platinum salts and has been used in organic synthesis. Therefore, we used K_2PtCl_4 as a pre-catalyst in the hydroarylation of propiolic acid (**2a**) with benzene (**1a**). The results are listed in Table 1.[12] The hydroarylation of **2a** with **1a** proceeded by using K_2PtCl_4/AgOTf catalyst to give (*Z*)-cinnamic acid selectively although the yield was low (Entry 1).[13] The yield was improved by elongation of reaction time (Entry 2). Using 6 equivalents of **1a** increased the yield (Entry 3). Furthermore, the elevation of temperature was effective, to give the best yield 61% in shorter reaction time (Entry 6). However, further increase of the amount of **1a** did not improve the yield (Entry 7). Entries 3 to 5 clearly show the effectiveness of K_2PtCl_4 among $Pd(OAc)_2$, $PtCl_2$, and K_2PtCl_4. The reaction using $PtCl_2$ was slower than that using K_2PtCl_4, while the reaction using $Pd(OAc)_2$ gave low yield because of low selectivity although the reaction was faster than Pt catalyst.

Table 1. Hydroarylation of propiolic acid with benzene[a]



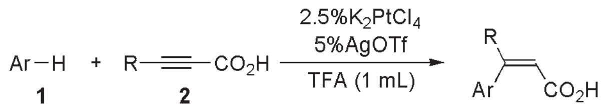
Entry	**1a** / equiv	Temp	Time/h	Yield/% (Z/E)[b]
1	3	rt	40	26 (100/1)
2	3	rt	70	50 (100/5)
3	6	rt	70	54 (100/1)
4	6	rt	70	35 (100/1)[c]
5	6	rt	10	11 (100/0.6)[d]
6	6	40 °C	40	61 (100/7)
7	12	40 °C	45	55 (100/2)

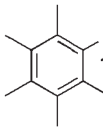
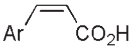
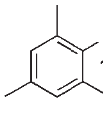
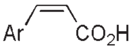
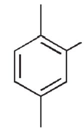
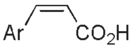
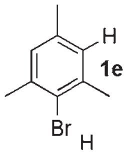
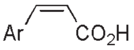
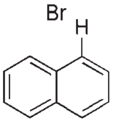
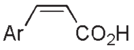
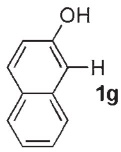
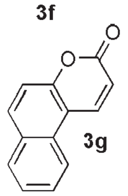
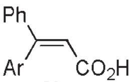
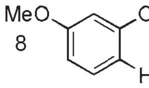
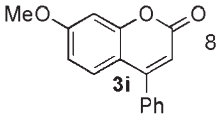
[a]Reaction conditions: K_2PtCl_4 (0.05 mmol), AgOTf (0.10 mmol), **1a** and **2a** (2 mmol), and TFA (1 mL). [b]Isolated yields based on **2a**. Z/E ratios were determined by ^{1}H NMR. [c]$PtCl_2$ (0.05 mmol) was used instead of K_2PtCl_4. [d]$Pd(OAc)_2$ (0.05 mmol) was used instead of K_2PtCl_4/AgOTf.

This Pt-catalyzed reaction was very efficient to various benzene derivatives (Table 2). The reactions of electron-donating, methyl-substituted arenes such as pentamethylbenzene (**1b**) and mesitylene (**1c**) proceeded smoothly even under milder conditions compared with the reaction of benzene, affording the corresponding cinnamic acids in high yields (Entries 1 and 2). Even the reaction of *p*-xylene (**1d**) afforded **3d** in more than 90% yield (Entry 3). Bromomesitylene (**1e**) having a bromine atom also gave **3e** in high yield although the reaction was conducted at 40 °C (Entry 4). Bromine is tolerable under the Pt catalysis. The reaction with 2-naphthol (**1g**) gave coumarin **3g** (Entry 6). In addition, a substituted propiolic acid, phenylpropiolic acid (**2b**, R = Ph), can be applied as an alkyne in the reaction. The reaction of **2b** with **1c** gave the corresponding cinnamic acid **3h** in high yield (Entry 7). The reaction of **2b** with 3-methoxyphenol (**1h**) afforded coumarin **3i** similar to the reaction of **2a** with **1g** (Entry 8).

In conclusion, we have demonstrated a new and efficient K_2PtCl_4/AgOTf catalyst for the hydroarylation of propiolic acids. The hydroarylation of propiolic acids gave predominantly (*Z*)-cinnamic acid derivatives in high yields. Noteworthy is a high activity of K_2PtCl_4/AgOTf catalyst toward less reactive benzene. Further studies on the scope of this hydroarylation using K_2PtCl_4/AgOTf are now in progress.

Table 2. Hydroarylation of propiolic acid with various arenes[a]



Entry	Ar−H	R	Temp	Time/h	Product and Yield/%[b]
1	 **1b**	H	rt	15	 **3b** 96[c]
2	 **1c**	H	rt	15	 **3c** 96
3	 **1d**	H	rt	25	 **3d** 93
4	 **1e**	H	40 °C	40	 **3e** 88[d]
5	 **1f**	H	40 °C	40	 **3f** 83[e]
6	 **1g**	H	rt	25	 **3g** 86[f]
7	**1c**	Ph	rt	40	 **3h** 86
8	 **1h**	Ph	rt	40	 **3i** 81[g]

[a]Reaction conditions: K_2PtCl_4 (0.05 mmol), AgOTf (0.10 mmol), arene **1** (6 mmol), propiolic acid **2** (2 mmol), and TFA (1 mL). [b]Isolated yield based on **2**. [c]**1b** (3 mmol) was used. CH_2Cl_2 (0.25 mL) was added. [d]CH_2Cl_2 (0.5 mL) was added. [e]**1f** (4 mmol) was used. $Cl(CH_2)_2Cl$ (0.75 mL) was added. [f]**1g** (4 mmol) was used. CH_2Cl_2 (0.75 mL) was added. [g]**1h** (4 mmol) was used. CH_2Cl_2 (0.5 mL) was used.

References and Notes

1 a) V. Ritleng, C. Sirlin, and M. Pfeffer, *Chem. Rev.*, **102**, 1731 (2002). b) G. Dyker, *Angew. Chem., Int. Ed. Engl.*, **38**, 1698 (1999). c) F. Kakiuchi and N. Chatani, *Adv. Synth. Catal.*, **345**, 1077 (2003). d) A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, **97**, 2879 (1997). e) C. Jia, T. Kitamura, and Y. Fujiwara, *Acc. Chem. Res.*, **34**, 633 (2001). f) F. Kakiuchi and S. Murai, *Acc. Chem. Res.*, **35**, 826 (2002). g) R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, **2001**, 2437. h) Y. Guari, S. Sabo-Etienne, and B. Chaudret, *Eur. J. Inorg. Chem.*, **1999**, 1047.

2 For recent review, see: C. Nevado and A. M. Echavarren, *Synthesis*, **2005**, 167.

3 a) B. M. Trost and F. D. Toste, *J. Am. Chem. Soc.*, **118**, 6305 (1996). b) B. M. Trost, F. D. Toste, and K. Greenman, *J. Am. Chem. Soc.*, **125**, 4518 (2003). c) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, and Y. Fujiwara, *Science*, **287**, 1992 (2000). d) C. Jia, D. Piao, T. Kitamura, and Y. Fujiwara, *J. Org. Chem.*, **65**, 7516 (2000). e) W. Lu, C. Jia, T. Kitamura, and Y. Fujiwara, *Org. Lett.*, **2**, 2927 (2000). f) J. Oyamada, C. Jia, Y. Fujiwara, and T. Kitamura, *Chem. Lett.*, **2002**, 380. g) T. Kitamura, K. Yamamoto, M. Kotani, J. Oyamada, C. Jia, and Y. Fujiwara, *Bull. Chem. Soc. Jpn.*, **76**, 1889 (2003). h) M. Kotani, K. Yamamoto, J. Oyamada, Y. Fujiwara, and T. Kitamura, *Synthesis*, **2004**, 1466. i) M. S. Viciu, E. D. Stevens, J. L. Petersen, and S. P. Nolan, *Organometallics*, **23**, 3752 (2004). j) N. Tsukada, T. Mitsuboshi, H. Setoguchi, and Y. Inoue, *J. Am. Chem. Soc.*, **125**, 12102 (2003).

4 a) C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, and Y. Fujiwara, *J. Am. Chem. Soc.*, **122**, 7252 (2000). b) J. Oyamada and T. Kitamura, *Tetrahedron Lett.*, **46**, 3823 (2005).

5 a) S. J. Pastine, S. W. Youn, and D. Sames, *Org. Lett.*, **5**, 1055 (2003). b) S. J. Pastine, S. W. Youn, and D. Sames, *Tetrahedron*, **59**, 8859 (2003).

6 a) M. T. Reetz and K. Sommer, *Eur. J. Org. Chem.*, **2003**, 3485. b) Z. Shi and C. He, *J. Org. Chem.*, **69**, 3669 (2004).

7 a) F. Kakiuchi, Y. Yamamoto, N. Chatani, and S. Murai, *Chem. Lett.*, **1995**, 681. b) P. W. R. Harris, C. E. F. Rickard, and P. D. Woodgate, *J. Organomet. Chem.*, **589**, 168 (1999).

8 F. Kakiuchi, T. Sato, T. Tsujimoto, M. Yamauchi, N. Chatani, and S. Muai, *Chem. Lett.*, **1998**, 1053.

9 Y.-G. Lim, K.-H. Lee, B. T. Koo, and J.-B. Kang, *Tetrahedron Lett.*, **42**, 7609 (2001).

10 T. Satoh, Y. Nishinaka, M. Miura, and M. Nomura, *Chem. Lett.*, **1999**, 615.

11 T. Tsuchimoto, T. Maeda, E. Shirakawa, and Y. Kawakami, *Chem. Commun.*, **2000**, 1573.

12 *General Procedure* for the K_2PtCl_4/AgOTf catalyzed hydroarylation of propiolic acid with arenes: A mixture of K_2PtCl_4 (0.05 mmol) and AgOTf (0.10 mmol) in trifluoroacetic acid (TFA) (1 mL) was stirred at room temperature for 10 min. An arene and propiolic acid were added to the mixture. Then, the mixture was stirred at the desired temperature. After a certain period, the reaction mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and washed with Et_2O (20 mL). Then, the ethereal layer was extracted with aq NaOH (10 mL × 3). The combined aqueous layer was washed with Et_2O (20 mL), acidified by aq HCl (ca. 36%) and extracted with CH_2Cl_2 (20 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo, affording cinnamic acids.

13 The use of 4 equivalents of AgOTf shortened the reaction time but did not improve the yield of products.

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