

## Palladium-catalysed dimerization of vinylarenes using indium triflate as an effective co-catalyst

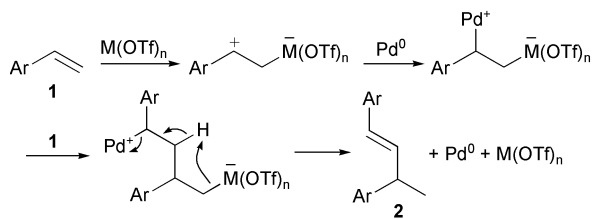
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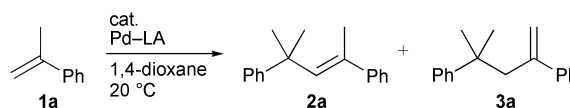
A palladium–indium triflate catalyst was found to be much more active for the dimerization of vinylarenes compared with generally used cationic palladium(II) catalysts.

Palladium complexes are powerful catalysts for carbon–carbon bond forming reactions because palladium(II) intermediates generated by oxidative addition of organic electrophiles to palladium(0) complexes can be utilized for wide scope of transformations such as transmetalation and insertion of unsaturated bonds.<sup>1</sup> However, organic electrophiles that can add oxidatively to palladium(0) complexes have been limited mainly to aryl/alkenyl halides/triflates.<sup>1</sup> Although the expansion of the scope by enhancing electrophilicity of organic compounds with Lewis acids has made a certain success, only substrates having a carbon–heteroatom bond have been used.<sup>2,3</sup> On the other hand, simple alkenes activated by Lewis acids are widely known to accept addition of relatively weak nucleophiles such as arenes, i.e., the Friedel–Crafts alkylation.<sup>4</sup> In this context, we have reported that metal triflates are efficient activators of alkynes and catalyse the Friedel–Crafts alkylation of arenes.<sup>5</sup> Thus we envisaged that metal triflates should activate vinylarenes to accept nucleophilic attack of palladium(0) complexes, giving oxidative adduct equivalents that accept insertion of another vinylarene as shown in Scheme 1. Here we report the palladium–indium triflate-catalysed dimerization of vinylarenes through nucleophilic attack of palladium(0) complexes to vinylarenes activated by indium triflate.



Scheme 1

We first examined the catalytic activity of Pd–In(OTf)<sub>3</sub> for the dimerization of  $\alpha$ -methylstyrene (**1a**) (Scheme 2 and Table 1). Treatment of **1a** with 1 mol % of Pd(OAc)<sub>2</sub><sup>6</sup> and 5 mol % of In(OTf)<sub>3</sub> in 1,4-dioxane at 20 °C for 3 h gave a mixture of (*E*)-4-methyl-2,4-diphenyl-2-pentene (**2a**) and 4-methyl-2,4-diphenyl-1-pentene (**3a**) in 78% yield with complete consumption of **1a** (entry 1).<sup>7</sup> Use of a catalytic amount of a phosphine such as PPh<sub>3</sub> or 1,3-bis(diphenylphosphino)propane (dppp) raised the yields in compensation for the reaction rate (entries 2–4). An *in situ* generated palladium(0) complex<sup>8</sup> coordinated by 2 equivalents of PPh<sub>3</sub> was also effective, whereas cationic Pd(II)–PPh<sub>3</sub> complexes, which are known to catalyse the dimerization of alkenes,<sup>9</sup> were totally inactive (entries 5–7). The use of Zr(OTf)<sub>4</sub> instead of In(OTf)<sub>3</sub> slightly lowered the yield, whereas metal chlorides failed to catalyse the dimerization (entries 8–11). Lack of a metal triflate or a palladium complex resulted in no or slow reaction, respectively (entries 12 and 13).



Scheme 2

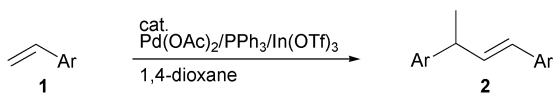
Table 1 Dimerization of  $\alpha$ -methylstyrene (**1a**) catalysed by Pd–Lewis acid<sup>a</sup>

Entry	Pd cat.	Additive (mol%)	Lewis Acid	Conv. (%) <sup>b</sup>	Yield (%) of <b>2a</b> + <b>3a</b> <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	none	In(OTf) <sub>3</sub>	> 99	78
2	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	In(OTf) <sub>3</sub>	> 99	86
3	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (2)	In(OTf) <sub>3</sub>	91	83
4	Pd(OAc) <sub>2</sub>	dppp (1)	In(OTf) <sub>3</sub>	92	92
5	Pd(0) complex <sup>c</sup>	PPh <sub>3</sub> (2)	In(OTf) <sub>3</sub>	70	41
6	[Pd(PPh <sub>3</sub> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	none	none	< 1	< 1
7	[( $\pi$ -C <sub>3</sub> H <sub>5</sub> )Pd(cod)]BF <sub>4</sub>	PPh <sub>3</sub> (2)	none	< 1	< 1
8	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	Zr(OTf) <sub>4</sub>	99	67
9	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	InCl <sub>3</sub>	11	< 1
10	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	AlCl <sub>3</sub>	< 1	< 1
11	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	TiCl <sub>4</sub>	< 1	< 1
12	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (1)	none	< 1	< 1
13	none	none	In(OTf) <sub>3</sub>	46	30

<sup>a</sup> The reaction was carried out in 1,4-dioxane (1.0 mL) at 20 °C for 3 h using **1a** (1.0 mmol) in the presence of a palladium catalyst (10  $\mu$ mol), an additive and a Lewis acid (50  $\mu$ mol). <sup>b</sup> Determined by GC. <sup>c</sup> A palladium(0) complex generated *in situ* by the reaction of [( $\pi$ -C<sub>3</sub>H<sub>5</sub>)PdCl]<sub>2</sub> with NaCH(CO<sub>2</sub>Me)<sub>2</sub> was used.<sup>8</sup>

The Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>/In(OTf)<sub>3</sub> (1/1/5) catalyst was successfully applied to the dimerization of various vinylarenes (Scheme 3 and Table 2). In addition to simple vinylarenes such as styrene (**1b**) and 2-vinylnaphthalene, styrenes bearing an electron-withdrawing group at the *para* position also dimerized to give 1,3-diaryl-1-butenes in high yields (entries 1–6). A styrene having a carboxyl group underwent the dimerization without protection (entry 4). Even aryl and benzyl halides, which are known to add to palladium(0) complexes, were tolerated (entries 5–7).<sup>1</sup> For the reaction of an electron-rich vinylarene, higher dilution that may prevent polymerization was required (entry 8). *o*-Divinylbenzene (**4**) underwent an intramolecular reaction to give 3-methylindene (**5**) in 73% yield, where CH<sub>3</sub>CN was a superior solvent to 1,4-dioxane (Scheme 4).

We had assumed that **1a** is more susceptible than **1b** to activation by Lewis acids because its methyl group would stabilize the resulting benzyl cation, whereas cationic H–Pd complexes, active species in the cationic palladium(II)-catalysed dimerization of alkenes,<sup>9</sup> prefer less bulky **1b** to **1a**. Thus, we examined the reaction with a 1 : 1 mixture of **1a** and **1b** using a Pd–In(OTf)<sub>3</sub> catalyst or a cationic Pd(II) catalyst and found that **1a** dimerized predominantly in the presence of the Pd–In(OTf)<sub>3</sub> catalyst, whereas a cationic complex catalysed the reaction of **1b** exclusively (Scheme 5). The different substrate preference in addition to the result that a palladium(0) is as effective as Pd(OAc)<sub>2</sub> (entries 3 and 5 of Table 1) should imply that a palladium(0) complex is included as an active species<sup>10</sup> in

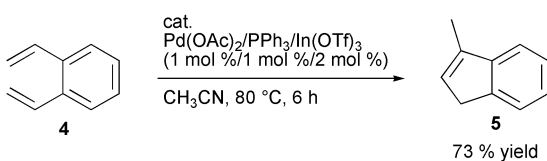


Scheme 3

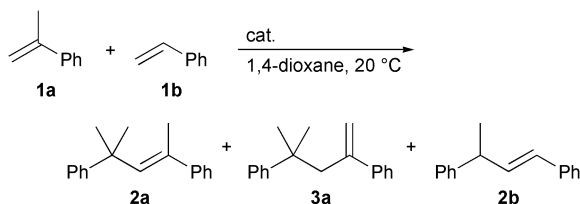
Table 2 Dimerization of vinylarenes catalysed by Pd–In(OTf)<sub>3</sub><sup>a</sup>

Entry	Ar	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Ph	20	3	98
2	2-Naphtyl	50	3	79
3	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	50	3	86
4	4-HOCO-C <sub>6</sub> H <sub>4</sub>	20	24	70
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	50	2.5	96
6	4-Br-C <sub>6</sub> H <sub>4</sub>	20	3	70
7	4-ClCH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	50	14	73
8 <sup>c</sup>	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	20	2	85

<sup>a</sup> The reaction was carried out in 1,4-dioxane (1.0 mL) using **1** (1.0 mmol) in the presence of Pd(OAc)<sub>2</sub> (10 μmol), PPh<sub>3</sub> (10 μmol) and In(OTf)<sub>3</sub> (50 μmol). <sup>b</sup> Isolated yield. <sup>c</sup> 1,4-Dioxane (5.0 mL) was used.



Scheme 4



cat. (Pd = 1 mol %)	time	conv. (%)		yield (%)	
		1a	1b	2a + 3a	2b
Pd(OAc) <sub>2</sub> /PPh <sub>3</sub> /In(OTf) <sub>3</sub> (1/1/5)	5 min	56	14	36	5
[Pd(PPh <sub>3</sub> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	40 h	0	62	0	51

Scheme 5

the present reaction not only in use of a palladium(0) complex as a precursor but also with Pd(OAc)<sub>2</sub>.<sup>11</sup>

In conclusion, we have disclosed that the novel catalyst system consisted of a palladium complex, PPh<sub>3</sub> and In(OTf)<sub>3</sub> is quite effective for the dimerization of vinylarenes. Studies on the details of the reaction mechanism as well as applications of the catalyst to various unreactive compounds are in progress in our laboratory.

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- It is well-known that palladium(II) complexes are reduced to palladium(0) species in the presence of an alkene. For example, see p 37 of reference 1.
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