

# Palladium-catalyzed cross-coupling reactions between organic tellurides and alkenes

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## Abstract

Diaryl tellurides, alkenyl aryl tellurides and dialkenyl tellurides react efficiently with various alkenes in methanol in the presence of a catalytic amount of PdCl<sub>2</sub> together with AgOAc and Et<sub>3</sub>N to give the corresponding aryl- and alkenyl-substituted alkenes with moderate to quantitative yields. Both monomeric and dimeric palladium complexes, (Ph<sub>2</sub>Te)<sub>2</sub>PdCl<sub>2</sub> and [(Ph<sub>2</sub>Te)PdCl<sub>2</sub>]<sub>2</sub> respectively, react readily with alkenes to give a high yield of phenyl-substituted alkenes. The key step of this coupling reaction is proposed to be the migration of an organic moiety from Te to Pd (transmetallation) in organic telluride–PdCl<sub>2</sub> complexes to afford organopalladium species.

*Keywords:* Alkene; Tellurium; Palladium; Catalysis

## 1. Introduction

It has been reported that various organic tellurides reacted with carbon monoxide in methanol in the presence of a catalytic amount of palladium(II) chloride (PdCl<sub>2</sub>) together with a reoxidant to afford the corresponding methyl carboxylates via an organopalladium intermediate formed in situ [1]. We thought that the intermediate might also react effectively with alkenes to afford alkene arylation products by the so-called Fujiwara–Heck coupling [2]. Therefore we attempted several reactions of organic tellurides (organotellurium(II) compounds) with alkenes in the presence of palladium(II) salt under various conditions and eventually found that the reaction system using PdCl<sub>2</sub> as a catalyst together with silver acetate (AgOAc) and triethylamine (Et<sub>3</sub>N) in methanol acted very efficiently for alkene arylation as well as alkene alkenylation. We report here the details of our results together with some mechanistic considerations. It is worth noting that, in contrast with palladium(II)-mediated and palladium(II)-catalyzed alkene arylation using organotellurium(IV) compounds [3], such a reaction with organic telluride

has only one precedent where diphenyl telluride reacted with ethyl acrylate in the presence of stoichiometric amount of Pd(OAc)<sub>2</sub> to give ethyl cinnamate [4].

## 2. Results and discussion

### 2.1. Coupling with diaryl tellurides

Treatment of diphenyl telluride (**1**) (X = H) with excess styrene (**2**) (R = Ph) in methanol at 25°C in the presence of a stoichiometric amount of palladium(II) acetate (to **1**) together with Et<sub>3</sub>N afforded (*E*)-stilbene with a good yield as expected from the literature [4]. In the absence of either Pd(OAc)<sub>2</sub> or Et<sub>3</sub>N the stilbene was not formed. Further studies disclosed that the reaction proceeded catalytically in palladium(II) salt such as PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> if a suitable oxidant such as AgOAc was added to the reaction system. Methanol and acetonitrile could be employed as solvent, but the reaction hardly occurred in other solvents such as tetrahydrofuran, benzene and acetic acid. Oxidants such as ammonium hexanitratocerate (CAN), CuCl<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were ineffective. Within our attempted experiments the optimum condition for the coupling in the following equation was revealed to be that using PdCl<sub>2</sub> (10 mol%; 0.1

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Table 1  
Coupling reaction of diaryl tellurides with alkenes <sup>a</sup>

Pd salt (equivalents)	Et <sub>3</sub> N (equivalents)	AgOAc (equivalents)	Telluride(1) X	Alkene(2) R	Products (%) <sup>b</sup>	
					3	4
Pd(OAc) <sub>2</sub> (1) <sup>c</sup>	2	0	H	Ph	40	Trace
PdCl <sub>2</sub> (0.1)	4	4	H	Ph	85	Trace
Pd(OAc) <sub>2</sub> (0.1)	4	4	H	Ph	79	Trace
Pd(OAc) <sub>2</sub> (0.1)	2	4	H	Ph	76	Trace
Pd(OAc) <sub>2</sub> (0.1)	2 <sup>d</sup>	2	H	Ph	43	Trace
Pd(OAc) <sub>2</sub> (0.1) <sup>e</sup>	4	4	H	Ph	75	Trace
PdCl <sub>2</sub> (0.1)	4	4	H	CO <sub>2</sub> Me	99	Trace
PdCl <sub>2</sub> (0.1)	4	4	H	CO <sub>2</sub> Et	99	Trace
PdCl <sub>2</sub> (0.1)	4	4	H	CN	67	22
PdCl <sub>2</sub> (0.1)	4	4	H	CHO	64	15
PdCl <sub>2</sub> (0.1)	4	4	H	CH <sub>2</sub> OAc	75	12
PdCl <sub>2</sub> (0.1)	4	4	H	C(O)Me	80	11
PdCl <sub>2</sub> (0.1)	4	4	CH <sub>3</sub>	Ph	73	10
PdCl <sub>2</sub> (0.1)	4	4	CH <sub>3</sub> O	Ph	99	Trace
PdCl <sub>2</sub> (0.1)	4	4	Br	Ph	99	Trace

<sup>a</sup> All the reactions were carried out in methanol at 25°C for 20 h using 0.5–1 mmol of **1** with 2 equivalents of alkene added to it.

<sup>b</sup> GLC yield; 2 mol equivalent of **3** to **1** and 1 mol equivalent of **4** to **1** correspond to 100% respectively.

<sup>c</sup> 20 equivalents of styrene were used.

<sup>d</sup> NaOH was used in place of Et<sub>3</sub>N.

<sup>e</sup> MeCN was used in place of MeOH.

equivalent to Ph<sub>2</sub>Te), Et<sub>3</sub>N (4 equivalents), AgOAc (4 equivalents) and methanol at 25°C for 20 h:

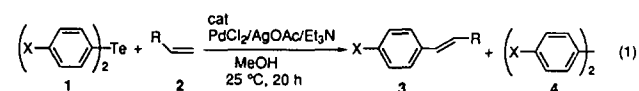


Table 1 summarized the results of application to various diaryl tellurides **1** (X = H, CH<sub>3</sub>, CH<sub>3</sub>O or Br) and electron-deficient alkenes **2** (R = Ph, CO<sub>2</sub>Me, CO<sub>2</sub>Et, CN, CHO, CH<sub>2</sub>OAc or C(O)Me) under this condition. The corresponding arylalkenes **3** were produced with a high yield (only the *E* isomer) in all cases together with biaryls **4** as minor products in some case. It is note

worthy that both aryl moieties of **1** were effectively used for the coupling.

## 2.2. Coupling with alkenyl tellurides

Next, such coupling reaction was attempted with alkenyl tellurides in place of diaryl tellurides under the above optimum condition. Several styryl tellurides such as (*Z*)- and (*E*)-phenyl styryl telluride **5** and **6**, and (*Z,Z*)-distyryl telluride (**7**) and (*E,E*)-distyryl telluride (**8**) were employed as alkenyl tellurides, while *p*-methylstyrene (**2**) (R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) was chosen as an alkene in place of styrene to distinguish clearly between homo-

Table 2  
Coupling reaction of various styryl tellurides with *p*-methylstyrene <sup>a</sup>

Pd salt (equivalents)	Et <sub>3</sub> N (equivalents)	AgOAc (equivalents)	Telluride	Products (%) <sup>b</sup>	
				9 ( <i>EE</i> ; <i>EZ</i> )	10 ( <i>E</i> )
PdCl <sub>2</sub> (1)	2	0	5	56 (27; 73)	28
PdCl <sub>2</sub> (0.1)	4	4	5	92 (23; 77)	57
Pd(OAc) <sub>2</sub> (0.1)	4	4	5	59 (30; 70)	67
Pd(OAc) <sub>2</sub> (0.1)	4 <sup>c</sup>	4	5	33 (20; 80)	— <sup>d</sup>
Pd(OAc) <sub>2</sub> (0.1)	2	2	5	60 (15; 85)	— <sup>d</sup>
PdCl <sub>2</sub> (0.1)	4	4	6	80 (77; 23)	44
PdCl <sub>2</sub> (0.1)	4	4	7	64 (39; 61)	—
PdCl <sub>2</sub> (0.1)	4	4	8	50 (68; 32)	—

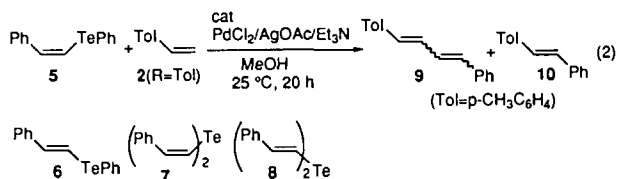
<sup>a</sup> All the reactions were carried out in methanol at 25°C for 20 h using 0.5 mmol of **5–8** and 2 equivalents of *p*-methylstyrene(**2**) (R = Ph) added to them.

<sup>b</sup> GLC yield: 1 mol equivalent of **9** and **10** to **5** and **6** corresponds to 100%; 2 mol equivalents of **9** to **7** and **8** corresponds to 100%.

<sup>c</sup> NaOH was used in place of Et<sub>3</sub>N.

<sup>d</sup> Not determined.

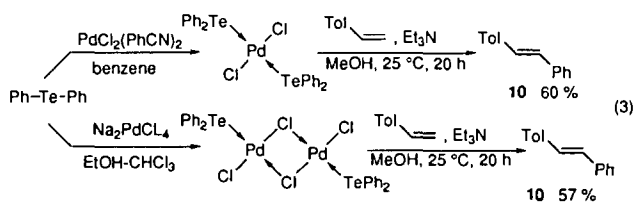
coupling and cross-coupling. The reaction proceeded smoothly to give the corresponding (*E,E*)- and (*E,Z*)-alkenylalkenes (**9**) and (*E*)-2-(*p*-methylphenyl)styrene (**10**) from **5** and **6** and only **9** from **7** and **8**:



Typical results of these are shown in Table 2. The former and the latter compounds were produced by coupling of **2** with the styryl part of **5** and with the phenyl part of **5** respectively. Under this condition the formation of homocoupling products such as 1,4-diphenyl-1,3-butadiene and biphenyl was not observed. As to the stereochemistry of **9** the configuration of the starting alkenyl tellurides was mainly retained as shown by *E,Z* rich (61–85%) from **5** and **7** and *E,E* rich (68–77%) from **6** and **8**. It has been reported that, in palladium(II)-mediated carbonylation, highly retentive reaction of **5** and **6** with carbon monoxide occurred with  $\text{Pd}(\text{OAc})_2$ , but the ratio of retention decreased much with  $\text{Li}_2\text{PdCl}_4$  especially from **5** [1c]. Several attempts to preserve the starting configuration of the tellurides completely in the products were unsuccessful. We confirmed separately that (*E,E*)-1,4-diphenyl-1,3-butadiene was completely recovered intact after treating it under conditions as similar as possible to those of the coupling reaction and that even at the initial stage of coupling the *E,E*-to-*E,Z* ratio of **9** is quite similar to that after 20 h. These results show that there is no isomerization between the *E,E* and *E,Z* isomers during the reaction and the ratio of *E,E* to *E,Z* is kinetically controlled.

### 2.3. Reaction scheme

It has been reported that carbonylation of monomeric and dimeric  $\text{PdCl}_2$ -diphenyl telluride complexes in methanol gave methyl benzoate with a good yield [1b,c]. It was disclosed that these complexes reacted also with *p*-methylstyrene (**2**) ( $\text{R} = \text{Ph}$ ) in methanol in the presence of  $\text{Et}_3\text{N}$  to afford the coupling product **10** with a good yield:

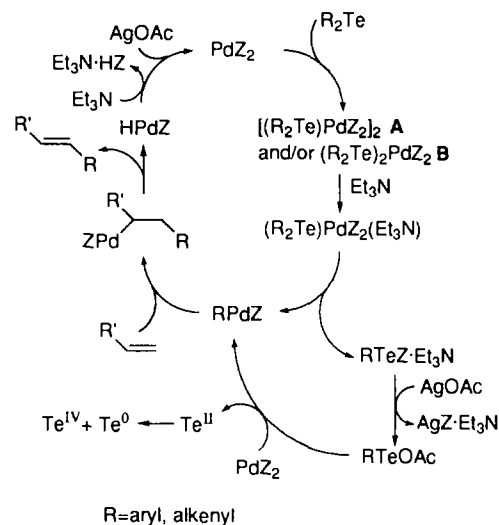


These results clearly show that one possible reaction

pathway for this coupling reaction involves the formation of an organic telluride–palladium(II) complex at the initial stage as has been proposed in palladium-catalyzed carbonylation of organic tellurides [1b,c]. After the formation of a dimeric complex **A** and/or a monomeric complex **B** (Scheme 1), aryl or alkenyl migration occurs to give aryl- or alkenyl-palladium species which react with alkenes to give arylalkenes or alkenylalkenes. Here, the stereochemistry of alkenylalkenes was not controlled in contrast with carbonylation case [1c]. Although the details are not yet known, the reaction of  $\text{RPdZ}$  with alkenes may be slower than that with  $\text{CO}$  to allow the isomerization in  $\text{RPdZ}$  ( $\text{R} = \text{alkenyl}$ ). The produced organotellurium species  $\text{RTeZ}$  may react with  $\text{PdZ}_2$  to give an organopalladium species  $\text{RPdZ}$  and inorganic  $\text{Te}(\text{II})$  species, the latter of which disproportionates to  $\text{Te}^0$  and inorganic  $\text{Te}(\text{IV})$  species. Both  $\text{Et}_3\text{N}$  and  $\text{AgOAc}$  played an important role for this catalytic coupling reaction. The former ( $\text{Et}_3\text{N}$ ) may act for the formation of new monomeric species having  $\text{Et}_3\text{N}$  as a ligand from **A** and/or **B** in which organic group transfer may be accelerated and also for the capture of  $\text{HCl}$  from  $\text{HPdCl}$  assisting the rapid formation of elemental palladium. The latter ( $\text{AgOAc}$ ) may work as a reagent, as well as the oxidant of elemental palladium to  $\text{Pd}(\text{II})$  species, for the formation of  $\text{PhTeOAc}$  from  $\text{PhTeZ} \cdot \text{Et}_3\text{N}$  which might react directly with  $\text{PdZ}_2$  by transmetalation to give an organopalladium species  $\text{RPdZ}$  of the catalytic cycle, furnishing both aryl or alkenyl groups of organic tellurides for the coupling.

### 3. Experimental details

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (400 and 100 MHz respectively) of the tellurides and the products (all are known)



$\text{R} = \text{aryl, alkenyl}$

Scheme 1.

were measured as solutions in  $\text{CDCl}_3$ . Melting points were uncorrected. Gas–liquid chromatography (GLC) analyses were performed on 1 m  $\times$  3 mm stainless steel column packed with 20% poly(ethylene glycol) on Shimalite and 25 m HiCap-CBP-10-S25 capillary column with flame ionization detectors and  $\text{N}_2$  as carrier gas. Column chromatographies on  $\text{SiO}_2$  were performed with Wakogel C-300 (hexane and hexane–ethyl acetate as eluents). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Commercially available organic and inorganic compounds were used without further purification. Solvents were distilled from  $\text{CaH}_2$  or  $\text{LiAlH}_4$  and stored over molecular sieves 4 Å under  $\text{N}_2$ . Diaryl tellurides **1** ( $X = \text{H}, \text{CH}_3, \text{CH}_3\text{O}$  or  $\text{Br}$ ) were prepared by the reported method [5]. The following organotellurium compounds were prepared by the reported methods respectively: (*Z*)- $\text{PhCH}=\text{CHTePh}$  [6], (*E*)- $\text{PhCH}=\text{CHTePh}$  [1c], (*Z,Z*)- $(\text{PhCH}=\text{CH})_2\text{Te}$  [7] and (*E,E*)- $(\text{PhCH}=\text{CH})_2\text{Te}$  [1d]. Authentic samples such as arylated alkenes, biaryl and (*E,E*)-1,4-diphenyl-1,3-butadiene for GLC analysis were commercial reagents. Other authentic samples of **9** ((*E,Z*), (*Z,Z*) and (*E,E*)) were prepared by treatment of the corresponding vinyl bromides with vinyl borates in the presence of palladium salt according to the reported method [8]. The retention time of each compound of **9** in GLC (25 m capillary column) was in the following increasing order: (*E,Z*) < (*Z,Z*) < (*E,E*). The monomeric and dimeric diphenyl telluride– $\text{PdCl}_2$  complexes were prepared by the reported method [1c]. A typical experimental procedure for the coupling reaction is as follows.

### 3.1. $\text{PdCl}_2$ -catalyzed coupling between di(*p*-methoxyphenyl) telluride and styrene

Into a two-necked 20 ml round-bottomed flask containing  $\text{PdCl}_2$  (8.8 mg, 0.05 mmol),  $\text{AgOAc}$  (388 mg, 2.00 mmol) and di(*p*-methoxyphenyl) telluride (171 mg, 0.50 mmol) were added dry methanol (10 ml),  $\text{Et}_3\text{N}$  (202 mg, 2.00 mmol) and styrene (104 mg, 1.00 mmol). After the heterogeneous reaction mixture had been stirred at 25°C for 20 h, the solid part was filtered. The filtrate was poured into brine (200 ml) and extracted with diethyl ether (50 ml  $\times$  3). GLC determina-

tion of the ether extract with diphenylmethane as an internal standard showed the presence of 0.99 mmol (99% yield) of (*E*)-*p*-methoxystilbene.

### 3.2. Treatment of $\text{PdCl}_2$ – $\text{Ph}_2\text{Te}$ complex with *p*-methylstyrene

To a round-bottomed flask containing  $(\text{Ph}_2\text{Te})_2\text{PdCl}_2$  (62 mg, 0.10 mmol) were added dry methanol (5 ml), *p*-methylstyrene (47 mg, 0.40 mmol) and  $\text{Et}_3\text{N}$  (81 mg, 0.80 mmol), and the mixture was stirred at 25°C for 20 h. The black precipitate formed was filtered and washed with diethyl ether (50 ml). The ether layer was washed with brine (200 ml) and dried over  $\text{MgSO}_4$ . The amount of product, (*E*)-*p*-methylstilbene (0.24 mmol) (60% yield) was determined by GLC with diphenylmethane as an internal standard.

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