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# CARBONYLATION OF ARYL- AND VINYL-TELLURIUM COMPOUNDS WITH CARBON MONOXIDE IN THE PRESENCE OF PALLADIUM(II) SALTS

KOUICHI OHE, HIDETAKA TAKAHASHI, SAKAE UEMURA* and NOBUYUKI SUGITA
*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 (Japan)*

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## Summary

Aryl- and vinyl-tellurium(II or IV) compounds react with carbon monoxide (CO) in suitable organic solvents to give the corresponding carboxylic acids in moderate to quantitative yields in the presence of a stoichiometric amount of a palladium(II) salt. Treatment of (*Z*)-styrylphenyl telluride with atmospheric pressure of CO at room temperature in the presence of palladium(II) chloride or lithium chloropalladate(II) affords predominantly (*E*)-cinnamic acid, while in the presence of palladium(II) acetate similar reaction gives the (*Z*)-acid highly selectively. Under higher CO pressures (5–50 atm), however, the (*Z*)-acid becomes the major product, even when palladium(II) chloride is used. The following pathways are proposed for this carbonylation: (1) in the first step organotellurium compounds form the monomeric and/or dimeric palladium complexes such as $[(R_2Te)PdCl_2]_2$ and/or $(R_2Te)_2PdCl_2$ (R = aryl, vinyl), then (2) the migration of R moiety from tellurium to palladium (transmetallation) occurs to afford the reactive aryl- or alkenyl-palladium compounds, and (3) the compounds react with CO to give the corresponding acylpalladium compounds, after alkaline hydrolysis, the carboxylic acids are formed. The presence of an ionic carbene-like organopalladium complex is proposed for the formation of the (*E*)-acid from (*Z*)-telluride.

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## Introduction

In recent years a number of synthetic reactions using organic and inorganic tellurium compounds have been developed [1–3], in which several methods for carbon–carbon bond formation have been developed. During the course of the investigation of functional group interconversion in organotellurium compounds [C–Te → C–X (X = halogen, oxygen, and any organic groups)] [4], we have found that some aryl- and vinyl-tellurium compounds react with carbon monoxide (CO) to give the corresponding carboxylic acids in the presence of a palladium(II) salt [5].

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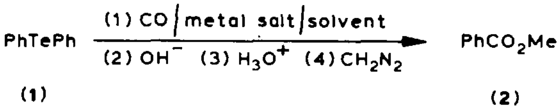
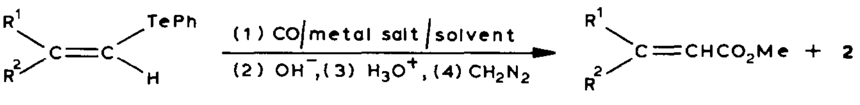
This reaction represents another example of the C–C bond formation using organotellurium compounds. We report here the details of this carbonylation. Of the group 16 elements, only tellurium shows this characteristic reaction, since the corresponding organo-sulfur and -selenium compounds scarcely afforded the carbonylation products under similar conditions. It is now known that various organometallic compounds of the group 12–15 elements react with CO in the presence of transition metal salts to give the corresponding carbonylation products, mostly via transmetallation [6].

## Results and discussion

Treatment of diphenyl telluride (**1**) with CO at atmospheric pressure and at room temperature in the presence of palladium(II) chloride and lithium chloride [lithium chloropalladate(II)] in acetonitrile followed by work-up (addition to aqueous NaOH and then neutralization with HCl), afforded benzoic acid together with a small amount of biphenyl. Ketones and aldehydes, e.g. benzophenone and benzaldehyde, were not detected among the products. The acid was generally determined by GLC as its methyl ester (**2**) after treatment with diazomethane. The best yield of acid was obtained when palladium(II) acetate was used, whereas the reaction hardly occurred with rhodium(III) chloride trihydrate or rhodium(I) carbonyl chloride. This CO insertion was also applicable to some vinyl tellurides such as styryl and l-octenyl phenyl tellurides (**3a, 3b, 3c**). Thus, from (*Z*)-styrylphenyl telluride (**3a**) *E* and *Z* isomers of methyl cinnamate (**4a**) and methyl benzoate (**2**) were obtained together with small amounts of biphenyl, stilbene and diphenyl telluride by use of lithium chloropalladate(II) or palladium(II) acetate. These carbonylations did not occur at all in the absence of palladium salt, even under 100 atm CO at 100 °C. Other transition metal salts such as those of nickel and platinum, palladium(0)- or -(II)-phosphine complexes were also shown to be ineffective for these carbonylations. The reaction did not proceed catalytically with a palladium(II) salt, since a molar ratio of the salt to the organotellurium compound was necessary to obtain good yields of carboxylic acids. From the results of the carbonylation of **3a, 3b**, and **3c** it was possible to deduce that the reactivity of a vinyl C–Te bond is much higher than that of a phenyl C–Te bond. Unfortunately, however, the reaction could not be applied to the alkenyl phenyl telluride containing ethoxycarbonyl or hydroxyalkyl moiety at the $\beta$-position to phenyltellurium moiety such as **3d** or **3e**, and none of the expected maleic acid esters or unsaturated $\gamma$-lactones were produced, even under higher pressure of CO, since benzoic acid was the sole product in each case. Typical results are summarized in Table 1. As can be seen from the table the starting telluride was generally not recovered even in cases where the yields of the expected products were very low. The apparent high conversion seems to be due to the coordination of transition metals or zerovalent metals with the starting telluride and/or the other telluride or ditelluride, which might be newly formed during the reaction, to give stable complexes, however attempts to isolate and characterize these complexes from the large amount of precipitated black solids which always resulted (IR active, but no $\nu$(C=O) absorption) were unsuccessful.

In the previously described carbonylation of **3a** and **3c**, both of which have the *Z*-configuration, we noticed that the steric configurations of vinylic acids (*E*- and *Z*-) depended on the type of palladium(II) salts; namely, lithium chloropalladate(II)





(**3a**: $R^1 = Ph, R^2 = H$;
**3b**: $R^1 = H, R^2 = Ph$;
**3c**: $R^1 = C_6H_{13}, R^2 = H$;
**3d**: $R^1 = CO_2Et, R^2 = H$;
**3e**: $R^1 = C(OH)Me_2, R^2 = H$)

(**4a**: $R^1 = Ph, R^2 = H$;
**4c**: $R^1 = C_6H_{13}, R^2 = H$)

and palladium(II) acetate assume the configuration of the *E*-isomer and the *Z*-isomer, respectively. This interesting stereochemical result prompted us to examine in more detail the relation between various reaction conditions (time, CO pressure,

TABLE 1

CARBONYLATION OF ARYL- AND VINYL-TELLURIUM COMPOUNDS WITH CO IN THE PRESENCE OF TRANSITION METAL SALT [a]

| Tellurium compound (1 mmol) | Transition metal salt [b] (mmol) | Conversion of **1** or **3** (%) [c] | Product yield (%) and isomer ratio [c] | |
|---|---|---|---|---|
| | | | **4**(*Z/E*) | **2** |
| **1** [d] | $RhCl_3 \cdot 3H_2O$ (1) | 100 | – | 9 |
| **1** [d] | $[Rh(CO)_2Cl]_2$ (1) | 10 | – | trace |
| **1** | $Li_2PdCl_4$ (2) | 100 | – | 58 [e] |
| **1** | $Pd(OAc)_2$ (2) | 100 | – | 85 [f] |
| **3a** | $NiCl_2$(1) | 4 | 0 | 0 |
| **3a** | $H_2PtCl_6 \cdot 6H_2O$ (1) | 84 | 0 | 0 |
| **3a** | $PdCl_2(PPh_3)_2$ (1) | – [g] | 0 | 0 |
| **3a** | $Pd(PPh_3)_4$ (1) | 50 | **4a** 10(50/50) | 9 |
| **3a** | $Li_2PdCl_4$ (1) | 100 | **4a** 83(34/66) | 10 |
| **3a** | $PdCl_2(0.2)/LiCl$ (2) | 58 | **4a** 90(22/78) | trace |
| **3a** | $Pd(OAc)_2$ (1) | 100 | **4a** 74(93/7) | 38 |
| **3b** [h] | $Li_2PdCl_4$ (1) | 100 | **4a** 41(1/99) | 12 |
| **3b** [h] | $Pd(OAc)_2$ (1) | 90 | **4a** 31(4/96) | 37 |
| **3c** [i] | $PdCl_2$ (1) | 100 | **4c** 52(27/73) [j] | 13 |
| **3c** [i] | $Pd(OAc)_2$ (1) [k] | 100 | **4c** 36(100/0) [l] | 48 |
| **3d** | $PdCl_2$ (1) | 100 | 0 | 10 |
| **3d** | $Pd(OAc)_2$ (1) | 100 | 0 | 29 |
| **3e** | $Li_2PdCl_4$ (1) | 100 | 0 | 11 |
| **3e** | $Pd(OAc)_2$ (1) [k] | 100 | 0 | 39 |

[a] Carried out in MeCN (10 ml) at 20–30 °C under 1 atm CO for 20 h unless otherwise stated. [b] $Li_2PdCl_4$ denotes a 1:2 mixture of $PdCl_2$ and LiCl. [c] Determined by GLC. The yield is based on the transition metal used. [d] THF as the solvent. [e] Other product; biphenyl (3%). [f] Other product; biphenyl (6%). [g] Not determined. [h] Contains 7% of **3a**. [i] Contains 27% $C_6H_{13}(PhTe)C{=}CH_2$. [j] Other product; $C_6H_{13}(MeO_2C)C{=}CH_2$ (25%). [k] Reaction time; 1.5 h. [l] Other product; $C_6H_{13}(MeO_2C)C{=}CH_2$ (15%).

TABLE 2

THE EFFECT OF REACTION TIME, CO PRESSURE, AND SOLVENT UPON CARBONYLATION OF **3a** [a]

| $Pd^{II}$ salt [b] (1 mmol) | Solvent (10 ml) | CO pressure (atm) | Reaction time (h) | Product yield(%) and isomer ratio ($Z/E$) [c] | |
|---|---|---|---|---|---|
| | | | | **4a** | **2** |
| $Li_2PdCl_4$ | MeCN | 1 | 1.5 | 84(38/62) | 8 |
| $Li_2PdCl_4$ | MeCN | 1 | 20 | 83(34/66) | 10 |
| $Li_2PdCl_4$ [d] | MeCN | 1 | 20 | 80(38/62) | 45 |
| $Li_2PdCl_4$ | MeCN | 1 | 40 | 81(36/64) | 18 |
| $Li_2PdCl_4$ | MeCN | 5 | 1.5 | 55(62/38) | 4 |
| $Li_2PdCl_4$ | MeCN | 20 | 1.5 | 68(68/32) | 5 |
| $Li_2PdCl_4$ | MeCN | 50 | 1.5 | 85(81/19) | 7 |
| $Li_2PdCl_4$ | THF | 1 | 24 | 59(5/95) | 4 |
| $Li_2PdCl_4$ | THF | 5 | 5 | 55(78/22) | 17 |
| $Li_2PdCl_4$ | THF | 20 | 5 | 49(84/16) | 12 |
| $Li_2PdCl_4$ | MeOH | 1 | 20 | 74(97/3) | 6 |
| $Li_2PdCl_4$ | acetone | 1 | 20 | 48(23/77) | 4 |
| $Li_2PdCl_4$ | $CHCl_3$ | 1 | 20 | 12(0/100) | trace |
| $PdCl_2$/LiCl(1) | MeCN | 1 | 20 | 65(20/80) | 6 |
| $PdCl_2$ | MeCN | 1 | 20 | 63(5/95) | 4 |
| $PdCl_2$ | MeCN | 20 | 20 | 77(66/34) | 15 |
| $PdCl_2(PhCN)_2$ | MeCN | 1 | 20 | 70(34/66) | 9 |
| $Pd(OAc)_2$ | MeCN | 1 | 20 | 74(93/7) | 38 |
| $Pd(OAc)_2$ | MeCN | 20 | 1.5 | 38(92/8) | 23 |
| $Pd(OAc)_2$/LiOAc(2) | MeCN | 1 | 20 | 43(98/2) | 33 |
| $Pd(OAc)_2$/HCl(2) [e] | MeCN | 1 | 20 | 80(79/21) | 7 |

[a] Carried out at 20–30 °C using **3a** (1 mmol) in a normal glass flask (1 atm CO) and a stainless steel autoclave with internal glass vessel. (5–50 atm CO). [b] $Li_2PdCl_4$ denotes a mixture of $PdCl_2$ (1 mmol) and LiCl (2 mmol). The amount of additive in mmol is in parentheses. [c] Determined by GLC. The yield is based on $Pd^{II}$ salt, namely 1 mmol of **4** or **2** corresponds to 100%. [d] 2 mmol. [e] Aqueous solution of HCl (36%) was employed.

solvent etc.) and the isomer ratio of the acids produced when **3a** is used as substrate. Typical results are shown in Table 2. The carbonylation using lithium chloropalladate(II) in acetonitrile was found to be complete within 1.5 h and that the yield and isomer ratio of cinnamic acids were scarcely affected by the reaction time or the amount of the palladium(II) salt, the *E*-isomer always predominating. When this reaction was carried out under higher pressures of CO (5–50 atm), the ratios of the *Z*-isomer increased when the pressure was increased. Thus, under 50 atm for 1.5 h the *Z*/*E* ratio was 81/19 compared with 38/62 under 1 atm, the product yield remained virtually the same. Similar dependence of the isomer ratios upon the CO pressure was also observed in THF solutions. On the other hand, the effect of pressure on isomer ratio was negligible when $Pd(OAc)_2$ was used. We confirmed separately that *Z*-cinnamic acid itself was not converted to the *E*-isomer under these carbonylation reaction conditions. The isomer ratio was also dependent on the type of solvent employed. Thus, the *E*-isomer was mainly obtained in THF, chloroform and acetone, and also in acetonitrile though the product yield was lower. On the other hand, the *Z*-isomer was formed highly selectively in methanol where only 20% of the product was the methyl ester, and the rest was free acid. The

TABLE 3

CARBONYLATION OF ARYLTELLURIUM(IV) CHLORIDES WITH CO IN THE PRESENCE OF PALLADIUM(II) SALT [a]

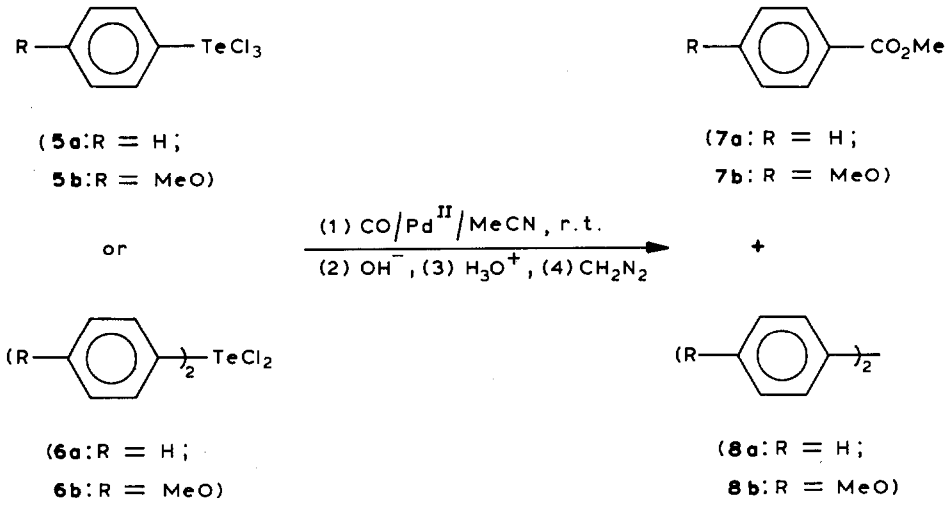
| Tellurium compound (1 mmol) | Pd(II) salt [b] (mmol) | CO pressure (atm) | Product and yield (%) [c] | |
|---|---|---|---|---|
| | | | 7 | 8 |
| **5a** | $Li_2PdCl_4$ (1) | 1 | **7a** 6 | **8a** 63 |
| **5a** | $Pd(OAc)_2$ (1) | 1 | **7a** trace | **8a** 55 |
| **5b** | $Li_2PdCl_4$ (1) | 1 | **7b** 3 | **8b** 40 |
| **5b** | $Li_2PdCl_4$ (1) | 20 | **7b** 8 | **8b** 41 |
| **5b** | $Pd(OAc)_2$ (1) | 1 | **7b** 2 | **8b** 27 |
| **5b** | $Pd(OAc)_2$ (1) | 20 | **7b** 7 | **8b** trace |
| **5b** | $PdCl_2(PhCN)_2$ (1) | 20 | **7b** 19 | **8b** 43 |
| **6a** | $Li_2PdCl_4$ (2) | 1 | **7a** 42 | **8a** 27 |
| **6a** | $Li_2PdCl_4$ (2) | 20 | **7a** 64 | **8a** 6 |
| **6a** | $Pd(OAc)_2$ (2) | 1 | **7a** 96 | **8a** 1 |
| **6a** | $Pd(OAc)_2$ (2) | 20 | **7a** 93 | **8a** trace |
| **6b** | $Li_2PdCl_4$ (2) | 1 | **7b** 36 | **8b** 57 |
| **6b** | $Li_2PdCl_4$ (2) | 20 | **7b** 41 | **8b** 11 |
| **6b** | $Pd(OAc)_2$ (2) | 1 | **7b** 43 | **8b** 14 |
| **6b** | $Pd(OAc)_2$ (2) | 20 | **7b** 57 | **8b** 11 |

[a] Carried out in MeCN (10 ml) at 20–30 °C in a normal glass flask (1 atm CO) and a stainless steel autoclave with internal glass vessel (20 atm CO) for 20 h. [b] $Li_2PdCl_4$ denotes a 1:2 mixture of $PdCl_2$ and LiCl. [c] Determined by GLC. The basis for the calculation of the yield is as follows: in the case of **5**, 1 mmol of **7** and 0.5 mmol of **8** correspond to 100% yield respectively, while in the case of **6**, 2 mmol of **7** and 1 mmol of **8** correspond to 100% yield respectively.

products obtained using methanol as the solvent is in sharp contrast to previously known palladium(II) or -(0) complex-catalyzed or -mediated carbonylation of organic halides and organometallic compounds in methanol where methoxycarbonylation leads to clean methyl ester formation [7]. As described above, the nature of the groups bound to palladium has a large effect on the stereochemistry of the products. This was further confirmed when we changed the amount of LiCl added to $PdCl_2$; the ratio of *Z*/*E* isomers of **4a** changed from 34/66 with $Li_2PdCl_4$ to 20/80 with $LiPdCl_3$, and to 5/95 with $PdCl_2$. In the case of $Pd(OAc)_2$ the addition of LiOAc decreased the product yield without appreciably affecting the isomer ratio, whereas the addition of HCl resulted in an increase of the *E*-isomer (93/7 → 79/21) without affecting the product yield. This increase in *E*-isomer yield may reflect the increased occurrence of $PdCl_2$ (from $Pd(OAc)_2$ and HCl) since $PdCl_2$ favors the formation of the *E*-isomer.

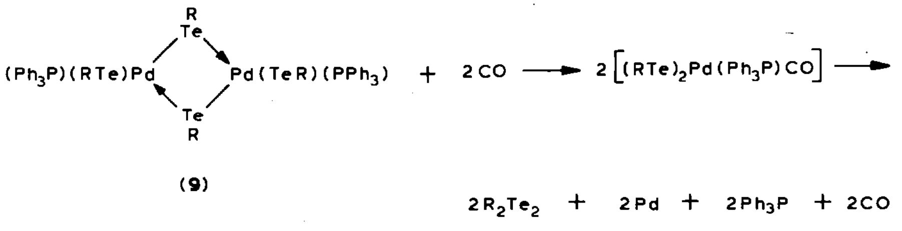
Next, this carbonylation reaction was applied to several readily available aryltellurium(IV) chlorides (**5** or **6**). The products were benzoic acid derivatives (**7**) and biaryl (**8**). Typical results are listed in Table 3. Carbonylation of aryltellurium trichlorides (**5**), led to compounds **7** and **8** which were the major and the minor products, respectively, irrespective of the type of palladium(II) salt and pressure of CO, whereas in the case of diaryltellurium dichlorides (**6**), compound **7** became the major product where the reaction at higher pressures of CO resulted in an increase in carboxylic acid yield by suppressing the formation of **8** as expected.

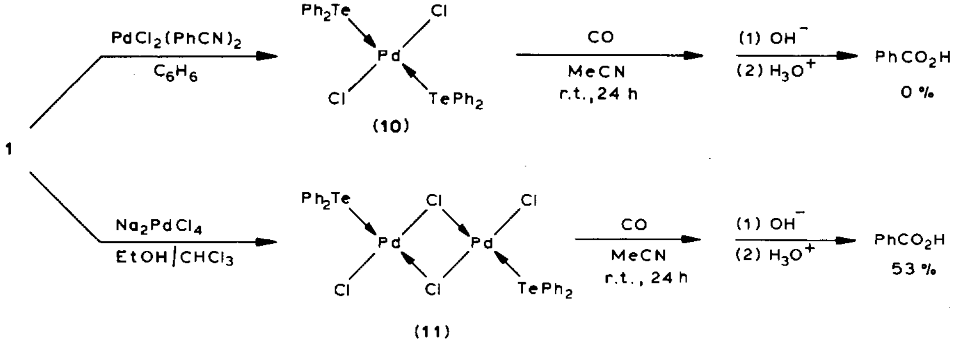
In sharp contrast to organotellurium compounds the corresponding organoselenium and -sulfur compounds afforded very little carboxylic acids or other



carbonylation products under similar reaction conditions. Thus, (*Z*)- and (*E*)-styrylphenyl selenide, diphenyl selenide, and diphenyl sulfide gave only 0–4% yields of cinnamic acid and/or benzoic acid using 1–20 atm of CO and $Li_2PdCl_4$ or $Pd(OAc)_2$ in acetonitrile for 20 h at room temperature. Similarly, in the case of diphenylselenium dichloride, benzoic acid and biphenyl were obtained in 1% and 6% yields and 14% and 1% yields by using $Li_2PdCl_4$ and $Pd(OAc)_2$, respectively, under at 1 atm of CO.

Since it has been found [8] that various organotellurium compounds, mostly dialkyl and diaryl tellurides, form monomeric and/or dimeric complexes with palladium(II) salts such as $(R_2Te)_2PdCl_2$ and/or $[(R_2Te)PdCl_2]_2$ (R = alkyl, aryl), it should be reasonable to assume that the present carbonylation reaction proceeds via such complexes. McWhinnie et al. [9] attempted reaction of a novel tellurium-bridged dimeric palladium complex (**9**) with CO and found that it decomposed into ditelluride, metallic palladium and phosphine. This is the only example of interaction between CO and an organic telluride-palladium complex, however in this case no CO insertion into the C–Te bond was observed. In order to obtain evidence to clarify our reaction pathway, we prepared some telluride-palladium complexes and attempted their carbonylations. A monomeric telluride-palladium complex (**10**) was prepared by the method of McWhinnie et al. [9] and its reaction with CO (1 atm) was carried out in acetonitrile at room temperature, but no benzoic acid was





produced. We then prepared a new chloro-bridged dimeric analogue of **10**, namely **11**, from **1** and sodium chloropalladate(II) by following the method of Chatt et al. [10]. Similar treatment of this complex with 1 atm CO afforded benzoic acid in 53% yield, this result agrees well with that of the direct carbonylation of **1** in the presence of palladium(II) and lithium chlorides.

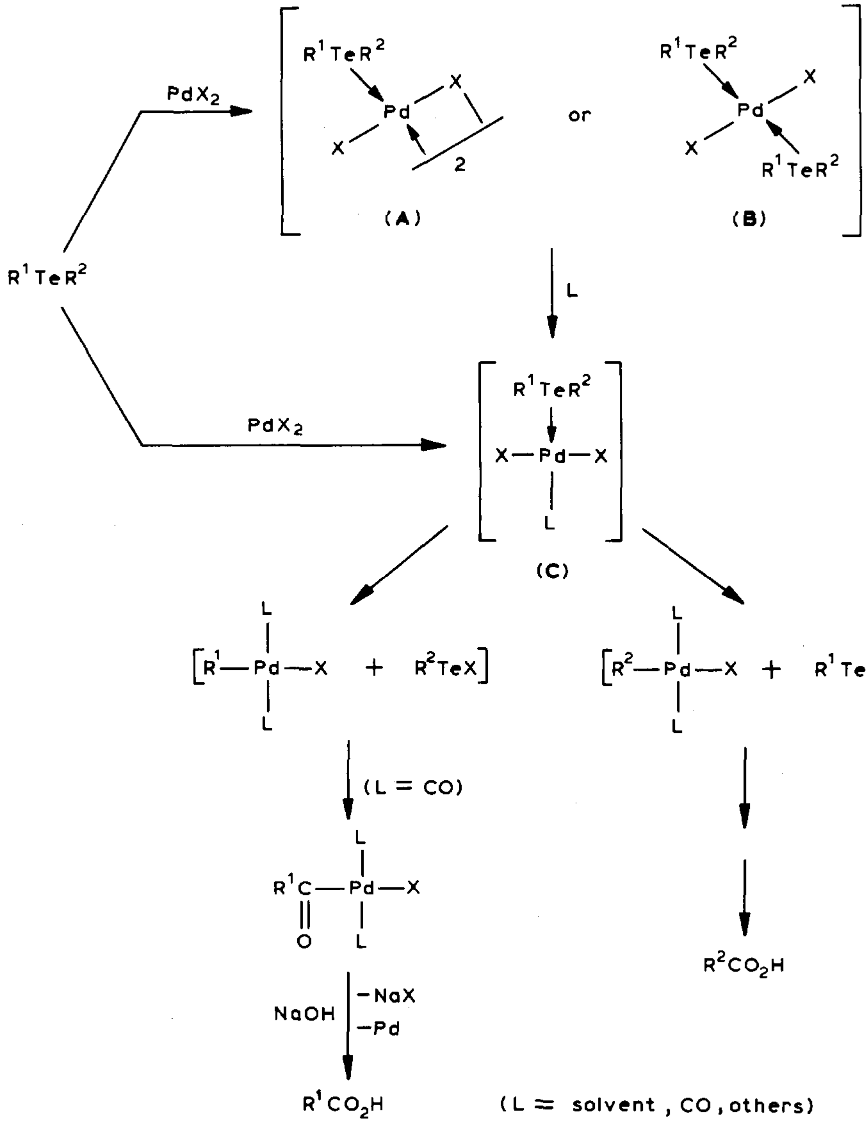
Similarly, we tried to prepare the complexes with the telluride, **3a**, and palladium(II) chloride, and succeeded in isolating a new monomeric complex (**12**). Interestingly, the reactivity of **12** to CO was somewhat different from that of **10**, since complex **12** reacted with CO(1 atm) in acetonitrile to give cinnamic acid (41%) of the isomer ratio Z/E = 41/59 together with the dissociated telluride, **3a** (19%).

$$\mathbf{3a} \xrightarrow[C_6H_6]{PdCl_2(PhCN)_2} \underset{(\mathbf{12})}{[(Z)\text{-}PhCH{=}CHTePh]_2PdCl_2} \xrightarrow[\text{r.t. } 20\text{ h}]{CO}_{MeCN} \xrightarrow[(2)\, H_3O^+ \\ (3)\, CH_2N_2]{(1)\, OH^-}$$

$$\underset{41\%(Z/E=41/59)}{PhCH{=}CHCO_2Me} + \underset{19\%}{(Z)\text{-}PhCH{=}CHTePh} + \underset{\text{trace}}{PhCO_2Me}$$

This isomer ratio roughly agrees with that ($Z/E = 34/66$) obtained by direct carbonylation of **3a** in the presence of $PdCl_2$ $(PhCN)_3$ in acetonitrile.

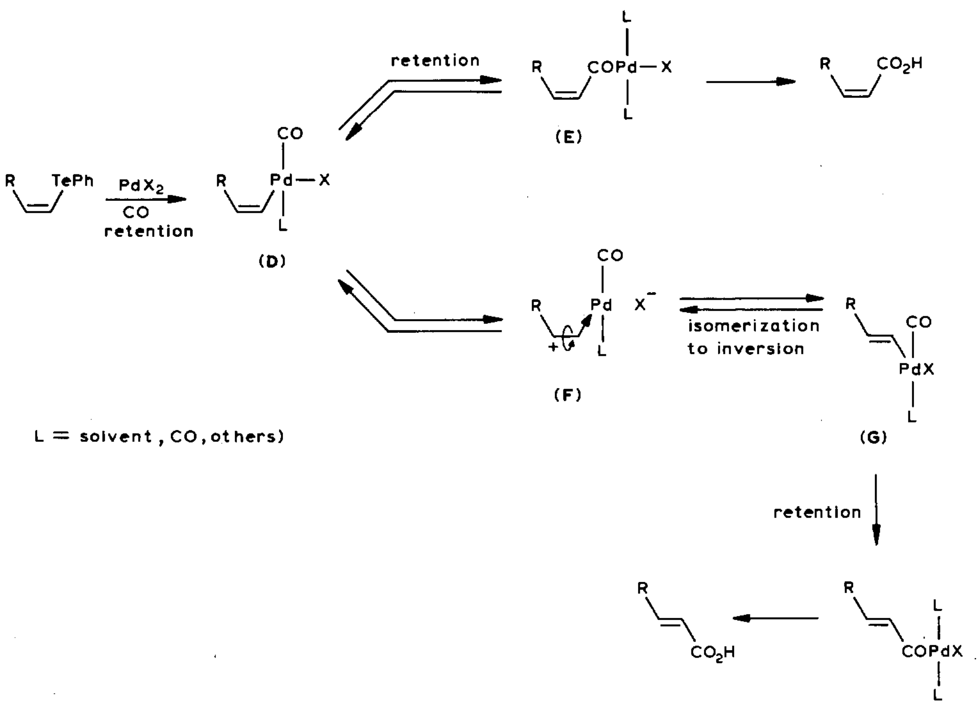
These results clearly show that one possible reaction pathway for this carbonylation involves the formation of an organic telluride-palladium complex, (**A**) or (**B**) (Scheme 1) as an initial step. The complex can be subsequently converted by the interaction of CO or solvent to complex **C** in which the organic moiety, $R^1$ or $R^2$, migrates from tellurium to palladium (transmetallation) to generate a reactive organopalladium species $R^1Pd(L_2)X$ or $R^2Pd(L_2)X$. Of course, direct formation of the complex **C** is also possible. Then CO insertion into the C–Pd bond of this organopalladium species occurs to give an acylpalladium species which is hydrolyzed to the carboxylic acid, the process is well known in organopalladium chemistry [7]. As described above, in this carbonylation methanol does not work well for direct methoxycarbonylation, which is in contrast to carbonylation by other organometallic compounds. One reason seems to be that when the acylpalladium species contains an organotellurium compound such as ditelluride, telluride, or organotellurenyl halide(PhTeX) etc. as ligand L, it may become too stable and so resistant to methanolysis, at room temperature, for steric and/or electronic reasons. The Te–Pd transmetallation which leads to the organopalladium species has already



SCHEME 1

been postulated for the olefin arylation and aromatic coupling by an organotellurium compound in acetic acid, in the presence of a palladium(II) salt [11].

Finally, we discuss the relationship between isomer ratios of the products (vinylic acids) and the reaction conditions. We have stated previously that neither *E*- nor *Z*-cinnamic acid isomerizes under our reaction conditions. It is well known that both transmetallation using palladium(II) salts of alkenylmetal compounds of such elements as Hg, B, Al, and Si [12] and CO insertion into a carbon–palladium bond proceed with retention of configuration [13]. Therefore, *Z*- and *E*-tellurides, should selectively afford *Z*- and *E*-acids, respectively, and this was actually found to be the case when palladium(II) acetate was used. Interestingly, in the case of palladium(II)



SCHEME 2

chloride a $Z/E$ mixture of acids occurring in various isomer ratios was obtained from $Z$-telluride. The results resemble those reported by Heck et al. [14] who treated *cis*- and *trans*-$\beta$-bromostyrene with CO in the presence of a catalytic amount of $PdBr_2(PPh_3)_2$ and obtained cinnamic acid as a $Z/E$ isomeric mixture and as the $E$-isomer alone, respectively. Taking into account these facts we propose the mechanism shown in Scheme 2 in order to explain the loss of configuration at the vinylic carbon during the carbonylation of the $Z$-tellurides, **3a** or **3c**. Te–Pd exchange began with retention of configuration to give a $\sigma$-vinylic palladium species with a CO ligand (**D**). This species then undergoes an intramolecular CO insertion with retention of configuration to give an acyl complex (**E**) leading in turn to the $Z$-acid. When X is Cl, the anion being a stronger base than the acetate anion, would cause complex **D** to form the ionic carbene-like intermediate (**F**) (as postulated by Heck et al. [14]) which then isomerizes to produce the thermodynamically more stable $\sigma$-vinylc palladium species (**G**) leading to the $E$-acid. Even in the case of X = Cl, when a higher pressure of CO was used, the rate of formation of complex **E** from complex **D** increased, resulting in the predominant formation of the $Z$-acid. The addition of LiCl can prevent the dissociation of chloride ion from complex **D** which then also leads to the favorable formation of the $Z$-acid. When the carbonylation (1 atm CO) of **3a** was carried out with $Pd(OCOCF_3)_2$ in MeCN at room temperature for 24 h, an isomeric mixture ($Z/E = 52/48$) of cinnamic acids was obtained in 27% yield. Although the yield was low, the isomer ratio was between 5/95 with $PdCl_2$ and 93/7 with $Pd(OAc)_2$. This order is in accord with the strength of the conjugate base $Cl^- > OCOCF_3^- > OAc^-$, supporting the assumption of the intermediacy of complex **F**.

## Experimental

$^1H$ NMR spectra were recorded with Hitachi Perkin–Elmer R600 (60 MHz), JEOL JNM FX-100 (100 MHz), and JEOLCO GX-400 (400 MHz) instruments (in $CDCl_3$ with $Me_4Si$ as an internal standard). $^{13}C$ NMR spectra were recorded with a Fourier transform NMR system (JNM FX-100) (in $CDCl_3$) after 250–1000 pulses with intervals of 2.7–2.8 s. GLC analyses were carried out by use of a Yanaco G2800 apparatus with Silicone DC QF-1 (5%)-Chromosorb-W (1m), PEG 6000 (25%)-Chromosorb-W (1 and 3m), and EGSS-X (3%)-Chromosorb-W(1m) columns ($N_2$ as carrier gas). IR spectra were recorded with Perkin–Elmer 521(4000–250 $cm^{-1}$) and JASCO IR-810(KBr, disk, neat, and paraffin mulls) spectrometers. Mass spectra were measured on a JEOL JMS-DS 300 mass spectrometer, equipped with a JMA-3500 data processing system, at the ionization voltage of 70eV. Melting points were determined with a Yanaco MP-S3 micro melting point determination apparatus, and were uncorrected.

### *Materials*

Diphenyl ditelluride was prepared by a published method involving the reaction of Te with PhMgBr [15], where irradiation with ultrasound reduces the reaction time significantly; namely from 24 h to 2 h. Commercially available Te, $TeCl_4$ (Nakarai Chemicals) and magnesium turnings (Wako Pure Chemical) were used without further purification, while commercial solvents were distilled immediately before use. The following organotellurium, -selenium, and -sulfur compounds were prepared by standard methods: **3a** [4a], **3d** [4a], **5a** [11], **5b** [11], **6a** [11], **6b** [11], (*Z*)-PhCH=CHSePh [16], (*E*)-PhCH=CHSePh [17]. Commercial diphenyl telluride (**1**), diphenyl selenide, diphenylselenium dichloride, and diphenyl sulfide were used without further purification. Dichlorobis(benzonitrile)palladium [18], tetrakis(triphenylphosphine)palladium [19], di(trifluoroacetato)palladium [20], and $[Rh(CO)_2Cl]_2$ [21] were prepared by published methods. Other transition metal salts such as $PdCl_2$, $Pd(OAc)_2$, $RhCl_3 \cdot 3H_2O$, $H_2PtCl_6 \cdot 6H_2O$, $NiCl_2$, and $Na_2PdCl_4$ were commercial products. Methyl esters, (*Z*)- and (*E*)-**4c**, (*E*)-**4a**, **7** and **8** were commercial products, while (*Z*)-methyl cinnamate [(*Z*)-**4a**] was isolated by column chromatography from the reaction products and identified by $^1H$ NMR; $\delta$(H) (100 MHz) 3.68 (3H, s), 5.92 (1H, d, *J* 12 Hz), 6.92 (1H, d, *J* 12 Hz), 7.0–7.6 (5H, m); the corresponding acid, $\delta$(H) (100 MHz) 5.97 (1H, d, *J* 12 Hz), 7.07 (1H, d, *J* 12 Hz), 7.2–7.7 (5H, m), 10.8 (1H, br, s) ppm.

### *Preparation of (Z)-1-octenyl phenyl telluride, 3c*

To a solution of diphenyl ditelluride (4.09 g, 10 mmol) in ethanol (20 ml) was added a solution of $NaBH_4$ (0.94 g, 25.0 mmol) in ethanol (20 ml) at room temperature under $N_2$. After a while the color of the solution turned from orange to pale yellow. A solution of 1-octyne (2.22 g, 20.2 mmol) in ethanol (10 ml) was then added to the pale-yellow solution and the mixture was stirred under reflux for 20 h. After it was cooled, the mixture was treated with brine, then extracted with $CHCl_3$ (3 × 50 ml), and the extract dried over $MgSO_4$. Evaporation of $CHCl_3$ left a red oil which was subjected to column chromatography on silica gel (hexane as eluent) to give a yellow liquid of a regioisomeric mixture (28/72 by GLC and $^1$H NMR) of $C_6H_{13}$(PhTe)C=$CH_2$ and **3c** (1.58 g, 5.0 mmol, 24.7%), **3c** being the major product. $\delta$(H) (100 MHz) of **3c** 0.90 (3H, t), 1.32 (8H, m), 2.0–2.4 (2H, m), 6.31 (1H, td, *J* 10.5 and 9.2 Hz), 6.72 (1H, dt, *J* 9.2 and 1.2 Hz), 7.08–7.34 (3H, m), 7.52–7.84 (2H, m); $\delta$(H) of $C_6H_{13}$(PhTe)C=$CH_2$ 5.42 (1H, s), 5.96 (1H, t, *J* 1.5 Hz) ppm. Anal. Found: C, 53.35; H, 6.24. $C_{14}H_{20}Te$ calc: C, 53.23; H, 6.38%.

*Preparation of (Z)-1-(3-methyl-3-hydroxy)butenyl phenyl telluride, 3e*

Similarly reaction with 3-hydroxy-3-methyl-1-butyne afforded a regioisomeric mixture (89/11 by GLC) of **3e** and $CH_2$=C(PhTe)C(OH)$Me_2$ in 76% yield: $\delta$(H) (100 MHz) of **3e** 1.36 (6H, s), 1.70 (1H, s), 6.42 (1H, d, *J* 10 Hz), 6.68 (1H, d, *J* 10 Hz), 7.10–7.29 (3H, m), 7.71–7.87 (2H, m); $\delta$(H) of $CH_2$=C(PhTe)C(OH)$Me_2$ 5.04 (1H, d, *J* 1.5 Hz), 5.95 (1H, d, *J* 1.5 Hz) ppm. Purification by column chromatography using hexane/ethyl acetate (5/1) as eluent afforded almost pure **3e** as a yellow solid; mp 51–53°C. Anal. Found: C, 45.56; H, 4.83. $C_{11}H_{14}OTe$ calcd.: C, 45.59; H, 4.87%.

*Preparation of (E)-styrylphenyl telluride, 3b*

To a mixture containing diphenyl ditelluride (2.10 g, 5 mmol) and Na wire (0.41 g, 8 mmol) in a two-necked 50-ml flask was added of hexamethylphosphoric triamide (HMPA) (40 ml) at room temperature and the resulting red suspension was stirred at 120°C for 1 h under $N_2$. (*E*)-$\beta$-Bromostyrene (1.86 g, 10 mmol), prepared by a published method [22], was then added and the mixture was stirred for a further 2 h at 120°C. After it had been cooled to room temperature, the mixture was treated with brine (200 ml), extracted with diethyl ether (3 × 50 ml), and the extract dried over $MgSO_4$. Removal of the solvent under reduced pressure left a red oily substance, GLC analysis of which showed that it consisted of unreacted diphenyl ditelluride and the expected telluride, **3b**. Since usual column chromatography on $SiO_2$ could not separate two compounds effectively, the diphenyl ditelluride in the mixture was converted to hexyl phenyl telluride by treatment with $NaBH_4$ (0.50 g, 13.2 mmol) and 1-bromohexane (0.88 g, 5.3 mmol) in EtOH (10 ml). After normal work-up [$CHCl_3$ (3 × 50 ml) extraction] evaporation of the solvent left a yellow-orange oil which was subjected to column chromatography on $SiO_2$ (hexane as eluent) to give 1.136 g (3.58 mmol, 34.4% yield) of **3b** as a yellow oil which contained a small amount of the (*Z*)-isomer, **3a** ($Z/E = 7/93$); $\delta$(H) (400 MHz) 7.11 (1H, d, *J* 17.1 Hz), 7.22–7.32 (8H, m), 7.55 (1H, d, *J* 17.1 Hz), 7.75 (2H, d, *J* 8.3 Hz); $\delta$(C) 101.4 (d, PhTeC=), 113.4 (s), 126.1 (d), 127.9 (d), 128.0 (d), 128.6 (d), 129.5 (d), 137.8 (d), 138.1 (s) 143.3 (d, PhC=) ppm; $\nu_{max}$ (neat) 3050, 3020, 2920, 1590, 1575s, 1565, 1495, 1470, 1445, 1435, 1320, 1300, 1205, 1160, 1060, 1020, 1000, 990, 960s, 900, 730s, 690, 650 cm$^{-1}$; $m/z$ (relative intensity) (only peaks stronger than 10% of the base peak above $m/z$ 50 are shown) 310 (*M*, 33.6), 308 (*M*, 29.9), 306 (*M*, 18.7), 181 (16), 180 (100), 179 (70), 178 (18), 103 (51), 102 (26), 78 (34), 77 (82), 51 (20). Anal. Found: C, 54.63; H, 3.92. $C_{14}H_{12}Te$ calc: C, 54.62; H, 3.90%.

*Carbonylation of organotellurium compounds*

Typical experimental procedure is shown below for the reaction of the telluride **3a**. In the case of normal pressure of CO, anhydrous lithium chloride (0.085 g, 2 mmol), palladium chloride (0.177 g, 1 mmol), and the telluride (0.308 g, 1 mmol) were placed in a two-necked 50 ml round bottom flask with a septum inlet and a three-way stopcock. The system was then flushed with CO from a CO balloon connected to the flask at room temperature, and dry solvent (10 ml) was added by a syringe. After the mixture had been stirred for 1.5–40 h at room temperature, during which black solids separated, it was poured into aqueous 1 *N* NaOH solution (100 ml) and stirred for another 30 min. The mixture was filtered through Celite and diethyl ether (100 ml) was added to the filtrate. Aqueous layer was separated off, acidified with hydrochloric acid, and then extracted with diethyl ether (3 × 30 ml). After the extract had been treated with diazomethane, the products were found to be the methyl esters of the acids (by GLC). In reactions using CO at higher pressures, a stainless steel autoclave (100 ml) with an internal glass vessel was used instead of the usual glass flask.

### *Synthesis of bis(diphenyl telluride)dichloropalladium, $(Ph_2Te)_2PdCl_2$, (**10**)*

A benzonitrile-$PdCl_2$ complex, $PdCl_2(PhCN)_2$, (0.38 g, 1 mmol) was dissolved in anhydrous benzene (100 ml) and the small amount of insoluble particles remaining, filtered off. To the resulting red-brown filtrate was added diphenyl telluride (0.57 g, 2 mmol), and the solution was stirred for 24 h at room temperature during which an orange solid separated. The solid product was removed, washed with hexane and dried in vacuo to give an orange powder, **10** (0.63 g, 0.84 mmol, 84%); mp 163–164° C (lit. [8], mp 164° C).

### *Synthesis of bis(diphenyl telluride)dichloro-μμ'-dichloropalladium, $[(Ph_2Te)PdCl_2]_2$, (**11**)*

To a solution of sodium tetrachloropalladate(II) (0.59 g, 2 mmol) in $CHCl_3$ was added a solution of diphenyl telluride (0.56 g, 2 mmol) in $CHCl_3$ (35 ml) and the mixture was stirred at room temperature for 1 d under $N_2$. The resulting brown solid was removed, washed with ethanol and dried. In addition a small quantity of it was recovered from the mother liquor. It was dissolved in hot $CHCl_3$ (400 ml) and the solution was filtered. The brown precipitate of **11** formed after the addition of hexane (1 l) to the filtrate. Filtration yielded **11** as a brown powder (0.62 g, 68%); mp 155° C(dec), $\nu_{max}$(KBr) 1570, 1480s, 1440s, 1330, 1310, 1180, 1160, 1060, 1020, 1000, 920, 845, 735s, 690s, 460, 445, 335 $cm^{-1}$. Anal. Found: C, 30.95; H, 2.11; Cl, 16.07. $C_{24}H_{20}Cl_4Pd_2Te_2$ calc: C, 31.39; H, 2.20; Cl, 15.44%.

### *Synthesis of bis((Z)-styrylphenyl telluride)dichloropalladium, $((Z)\text{-}PhCH{=}CHTePh)_2\text{-}PdCl_2$, (**12**)*

To a (red-brown) benzene solution (100 ml) of $PdCl_2(PhCN)_2$ (0.38 g, 1 mmol), prepared as described above, was added **3a** (0.62 g, 2 mmol) and the mixture was stirred for 92 h at room temperature. The reaction mixture was then warmed up to 70° C and the hot solution was quickly added to petroleum ether (200 ml) and the mixture was cooled on standing. An orange precipitate which gradually separated, was collected by filtration, washed with a small amount of petroleum ether, and then dried in vacuo to afford an orange solid, **12**, (0.43 g, 0.54 mmol, 54%): mp 114–115.5° C; $\nu_{max}$ (KBr) 1580, 1565, 1480, 1470, 1440, 1435, 1320, 1300, 1290, 1170, 1060, 1015, 995, 910, 810, 765s, 740s, 700, 680, 650, 495, 470, 440, 365, 340 $cm^{-1}$; δ(H) (400 MHz) 7.14 (1H, d, J 10.0 Hz), 7.30–7.45 (8H, aromatic, m), 7.64

(1H, d, $J$ 10.0Hz), 7.93 (2H, aromatic, d, $J$ 7.3 Hz) ppm. Anal. Found: C, 42.02; H, 2.89; Cl. 8.97. $C_{28}H_{24}Cl_2PdTe_2$ calcd.: C, 42.57; H, 3.06; Cl, 8.98%.

### *Reaction of the complexes **10** and **11** with CO*

Complex **10** (0.38 g, 0.5 mmol) was placed in a round bottom flask (with a septum inlet) and the system was flushed with CO from a balloon connected to the flask. Dry acetonitrile (5 ml) was then added by a syringe, and the mixture stirred for 20 h at room temperature. The unchanged orange solid of **10** (0.35 g, mp 162° C) was filtered and the filtrate was poured into an aqueous 1 *N* NaOH solution (100 ml) and extracted with diethyl ether (3 × 30 ml). GLC analysis of the extract revealed the presence of biphenyl (trace) and benzophenone (0.03 mmol). The aqueous layer was acidified with hydrochloric acid and extracted with diethyl ether (3 × 30 ml) and the extract was treated with diazomethane, GLC analysis of which showed a complete absence of the expected methyl benzoate. The reaction of complex **11** (0.46 g, 0.5 mmol) with CO was carried out in MeCN (10 ml) in a similar way to the above, GLC analysis showing the presence of methyl benzoate (0.53 mmol, 53%) together with small amounts of diphenyl telluride, biphenyl, and benzophenone.

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