106-26-3; **3i**, 14371-10-9; **4**, 78091-18-6; **5**, 2171-98-4; **6a**, 598-32-3; **6b**, 4798-44-1; **6c**, 3391-86-4; **6d**, 3899-34-1; **6e**, 4325-82-0; **6f**, 822-67-3; **6g**, 470-99-5; **6h**, 26675-10-5; **6i**, 36004-04-3; **6j**, 79380-04-4; **7a**, 78-94-4; **7b**, 1629-60-3; **7c**, 4312-99-6; **7d**, 3102-33-8; **7e**, 141-79-7; **7f**, 930-68-7; **7g**, 78-59-1; **7h**, 826-56-2; **7i**, 1896-62-4; **7j**, 41438-24-8; **8a**, 6278-91-7; $ZrCl_4$, 10026-11-6; Na(O-*i*-Pr), 683-60-3; butanal, 123-72-8; octanal, 124-13-0; furfural, 98-01-1; acetone, 67-64-1; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; benzophenone, 119-61-9; 2,6-dicinnamylidenecyclohexanone, 18977-40-7.

Palladium(II) Chloride Catalyzed Carbonylation of Organic Tellurides with Carbon Monoxide

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Various organic tellurides react with carbon monoxide (1 atm) at room temperature in methanol in the presence of $PdCl_2$ and Et_3N to afford the corresponding methyl carboxylates in good to excellent yields. The reaction is catalytic in $PdCl_2$ when a suitable reoxidant such as $CuCl_2$, $CuCl/O_2$, $FeCl_3$, or $Ce(NH_4)_2(NO_3)_6$ is present. The combination of this carbonylation with phenyltellurenylation of arylacetylenes and propargylic alcohols makes it possible to prepare ring-substituted *cis*-methyl cinnamates and $\Delta^{\alpha,\beta}$-butenolides, respectively. Both monomeric and dimeric palladium complexes, $(Ph_2Te)_2PdCl_2$ and $[(Ph_2Te)PdCl_2]_2$, react readily with CO to give a high yield of methyl benzoate. The key step of the present carbonylation is proposed to be the migration of an organic moiety from Te to Pd (transmetalation) in organic telluride–$PdCl_2$ complexes, presumably formed in situ, to afford organopalladium compounds.

We previously reported that some organotellurium (II or IV) compounds reacted with carbon monoxide (CO) in various organic solvents to give the corresponding carboxylic acids in moderate to quantitative yields in the presence of $PdCl_2$, $PdCl_2/LiCl$, or $Pd(OAc)_2$.[1,2] This was a characteristic reaction of tellurium among the group 16 elements, since the corresponding organosulfur and -selenium compounds scarcely afforded the carbonylation products under similar conditions. In this carbonylation, however, there were several disadvantages as follows: (1) a stoichiometric amount of Pd(II) salt was necessary; (2) after the reaction, an alkaline hydrolysis was needed to obtain the expected acid, and a generally known methoxycarbonylation giving directly its methyl ester occurred only partly even in methanol as the solvent; (3) the kind of organotellurium substrates that can be carbonylated was limited. We attempted to improve this reaction and eventually found that methoxycarbonylation occurs readily for a wide range of organic tellurides under 1 atm CO in methanol when triethylamine was added as a base to the reaction system and the reaction is catalytic in $PdCl_2$ in the presence of a suitable reoxidant. We could prepare *cis*-cinnamates and butenolides from the appropriate acetylenes by the following transformation, and the method may be of interest since the formal addition of PhTeH to acetylenes is facile and highly regio- and stereoselective.[3] The details of the results are herein reported.

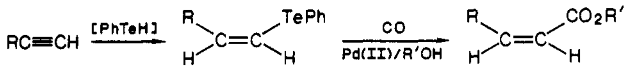

Table I. Carbonylation of Organotellurium Compounds[a]

Te compound	Pd(II)/ additive[b]	product, % yield[c]	
1a	A	**2a**, 96	**3**, 30
1a	B	**2a**, 44[d]	**3**, 6[d]
1a	C	**2a**, 28[e]	**3**, 4[e]
1a	D	**2a**, 48	**3**, 24
1b	A	**2b**, 71	**3**, 24
1c	A	**2c**, 72	**3**, 32
1d	A	**2d**, 67	**3**, 17
1f	A	**3**, 92	
1f	E	**3**, 96	
$(4\text{-}MeOC_6H_4)_2Te$	A	**2**,[f] 99	
$(4\text{-}MeOC_6H_4)_2TeCl_2$	A	**2**,[f] 18	
1g	E	**2g**, 22[g]	**3**, 98[g]
5a	A	**6a**, 22[h]	**3′**,[i] 8
5b	A	**6b**, 51[h]	**3′**, 3
5c	A	**6c**, 43[h]	**3′**, 21
5d	A	**6d**, 0	**3′**, 25
5e	A	**6e**, tr	**3′**, 24

[a] Carried out with organotellurium compound (1 mmol) and 1 atm CO in MeOH (10 mL) at 25 °C for 5 h to obtain **2** or in CH_2Cl_2 (10 mL) at 5–10 °C for 20 h to obtain **6**. [b] Key: A, $PdCl_2$ (1 mmol)/Et_3N (2 mmol); B, $PdCl_2$ (1 mmol)/NaOAc (2 mmol); C, $PdCl_2$ (1 mmol); D, $Pd(OAc)_2$ (1 mmol)/Et_3N (2 mmol); E, $PdCl_2$ (2 mmol)/Et_3N (4 mmol). [c] GLC yield based on Pd(II) salt. [d] Other products: cinnamic acid (46%, Z/E = 97/3) and benzoic acid (11%). [e] Other products: cinnamic acid (44%, Z/E = 100/0) and benzoic acid (8%). [f] R = $4\text{-}MeOC_6H_4$. [g] The yield is based on **1**; other product, 1-dodecene (37%). [h] Isolated yield based on Pd(II) salt. [i] **3′** = $PhCO_2H$.

Results and Discussion

On treatment of (*Z*)-styryl phenyl telluride (**1a**) with atmospheric pressure of CO and a stoichiometric amount of $PdCl_2$ in methanol in the presence of triethylamine at 25 °C for 5 h, (*Z*)-methyl cinnamate (**2a**) and methyl benzoate (**3**) were obtained in 96% and 30% yields, respectively (eq 1). When sodium acetate was used as a base in place of triethylamine, about half of the products was obtained in acid form (*cis*-cinnamic acid and benzoic acid). In the absence of base the product yield was slightly lower, and the product was mainly obtained as the acid form. The reaction using $Pd(OAc)_2$ and triethylamine gave products completely as methyl esters, but their yields were

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(1) Uemura, S.; Ohe, K.; Kim, J.-R.; Kudo, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.* **1985**, 271.

(2) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1987**, *326*, 35.

(3) (a) Buzilova, S. R.; Vereshchagin, L. I.; Sadekov, I. D.; Minkin, V. I. *Zh. Obshch. Khim.* **1976**, *46*, 932; *Chem. Abstr.* **1976**, *85*, 20761g. (b) Buzilova, S. R.; Sadekov, I. D.; Lipovich, T. V.; Fillipova, T. M.; Vereshchagin, L. I. *Zh. Obshch. Khim.* **1977**, *47*, 1999; *Chem. Abstr.* **1978**, *88* 22289v. (c) Uemura, S.; Fukuzawa, S.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9. (d) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875. (e) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V.; Petragnani, N. *J. Organomet. Chem.* **1986**, *308*, 211. (f) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *Nippon Kagaku Kaishi* **1987**, 1508.

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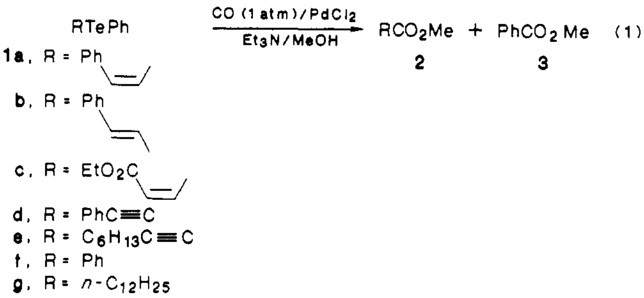

lower than the case of $PdCl_2/Et_3N$. In all cases a black precipitate deposited during the reaction. Other transition-metal chlorides such as Ru(III), Rh(III), and Ir(III) were revealed to be ineffective; thus, the $RhCl_3{\cdot}3H_2O/Et_3N$ system afforded only 5% of **2a** under similar conditions despite 100% conversion of **1a**, while the $RuCl_3/Et_3N$ and $IrCl_3/Et_3N$ systems did not afford any carbonylation products, and almost all of **1a** was recovered intact. Since the $PdCl_2/Et_3N/MeOH$ system was revealed to be the best among the systems examined for methoxycarbonylation, we applied this reaction system to several alkynyl-, alkenyl-, aryl-, and alkyltellurium compounds and succeeded in obtaining the corresponding methyl esters directly (Table I). The carbonylation proceeded with complete retention of configuration in alkenyltellurium compounds. In the case of dodecyl phenyl telluride (**1g**), the formation of a considerable amount of 1-dodecene was observed beside the expected methyl ester. The olefin formation seems to be due to a β-hydride elimination from the dodecylpalladium(II) intermediate, and it was not possible to avoid this under several reaction conditions examined. Although it has been known that $PdCl_2$-mediated methoxycarbonylation of bis(phenylethynyl)mercury with 20 atm CO gave mainly dimethyl phenylmaleate together with small amounts of **2d** and dimethyl phenylfumarate,[4] no maleate and fumarate were observed in the products in the carbonylation of **1d**. When bis(phenylethynyl)mercury was treated under our conditions (1 atm $CO/PdCl_2/Et_3N$), only **2d** was formed in a low yield (~7%).

This type of chemistry could be extended to the synthesis of butenolides by tellurenylation of propargylic alcohols 4, followed by carbonylation (eq 2). Thus, phenyltellurenylation of 4 always gave a regioisomeric mixture of (*Z*)-alkenyl tellurides (**5**) and $R^1(R^2)C(OH)C(TePh){=}CH_2$ (**5′**) (95–80:5–20) in 70–80% yield,[5] and carbonylation of **5** in nonpolar solvents such as chloroform and dichloromethane at low temperature afforded the corresponding $\Delta^{\alpha,\beta}$-butenolides **6** in moderate yields. In methanol as solvent, neither methoxycarbonylation nor lactonization proceeded appreciably. For such lactonization the presence of both substituents (R^1 and R^2) at the allylic carbon of **5** was essential, and thus none of **6** was obtained from **5d** and **5e**. Typical results are also listed in Table I.

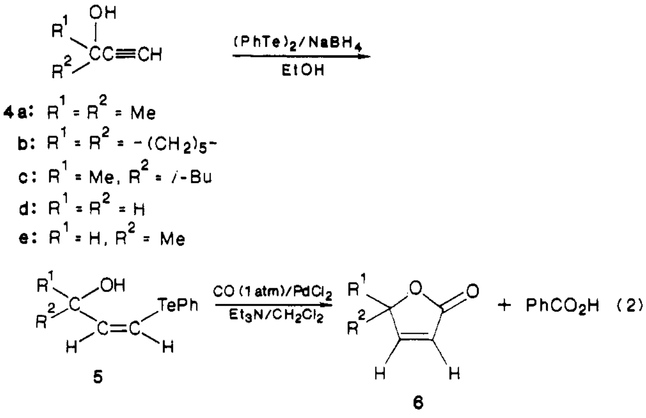

Table II. $PdCl_2$-Catalyzed Carbonylation of Organic Tellurides[a]

organic telluride	reoxidant	% convn of telluride[b]	product % yield[c]
1a	$CuCl_2$	92	**2a** 86 (861)
1a	$CuCl/O_2$[d]	89	**2a** 78 (781)[e]
1a	$FeCl_3$	64	**2a** 46 (458)
1a	$Ce(NH_4)_2(NO_3)_6$	46	**2a** 38 (384)
1a	*p*-benzoquinone	33	**2a** 13 (127)
1d	$CuCl_2$	100	**2d** 60 (600)[f]
1e	$CuCl_2$	100	**2e** 37 (370)[g,h]
1f	$CuCl_2$	92	3 23 (450)
$(4\text{-}MeOC_6H_4)_2Te$	$CuCl_2$	90	2[i] 24 (470)
5b	$CuCl_2$	–[j]	**6b** 21 (209)
5c	$CuCl_2$	–[j]	**6c** 23 (232)
8a	$CuCl_2$	77	**9a** 60 (596)[g]
8b	$CuCl_2$	96	**9b** 73 (732)[g]
8c	$CuCl_2$	86	**9c** 71 (713)[g]
8d	$CuCl_2$	95	**9d** 80 (798)[g]

[a] Carried out with organic telluride (1 mmol), $PdCl_2$ (0.1 mmol), Et_3N (2–3 mmol), and reoxidant (2 mmol) in MeOH (10 mL) at 25 °C for 75 h under 1 atm CO. With **5b** and **5c**, carried out in CH_2Cl_2 (10 mL) at 5 °C. [b] Determined by GLC. [c] GLC yields based on a telluride unless otherwise stated. The yields based on Pd(II) are shown in parentheses. The *Z*/*E* ratios of **2** and **9** are 100/0. [d] CuCl (1 mmol)/O_2 (1 atm). [e] *Z*/*E* = 97/3. [f] Other product: $(PhC{\equiv}C)_2$, 0.2 mmol. [g] Isolated yield. [h] Other product: $(C_6H_{13}C{\equiv}C)_2$, 0.15 mmol. [i] R = $4\text{-}MeOC_6H_4$. [j] Not determined.

This carbonylation was revealed to be catalytic in palladium(II) when a reoxidant such as copper(II) chloride, copper(I) chloride/oxygen, iron(III) chloride, cerium(IV) ammonium nitrate, or *p*-benzoquinone was added to the reaction system, copper(II) chloride being most effective among the oxidants examined (Table II). In contrast to the stoichiometric reaction, a side product **3** was scarcely formed (at most a 3% yield based on the telluride) in the catalytic reactions of alkenyl and alkynyl phenyl tellurides. In the carbonylation of alkynyl phenyl tellurides using the $PdCl_2/CuCl_2/Et_3N$ system, the formation of coupling products, bis(alkynyls), was always observed. We confirmed separately that these coupling compounds were produced even without $PdCl_2$ and that CuCl instead of $CuCl_2$ was not effective at all for the coupling. For the preparation of $\Delta^{\alpha,\beta}$-butenolide Larock[6] reported an effective Pd(II)- or Pd(0)-catalyzed lactonization of (β-chlorovinyl)mercury compounds obtained by trans addition of $HgCl_2$ to propargylic alcohols. Also, Stille has shown a facile lactonization of vinylic iodides catalyzed by Pd(II) or Pd(0).[7] In our case, however, the catalytic lactonization did not proceed effectively. The catalytic reaction could be applied well to stereoselective synthesis of various ring-substituted methyl *cis*-cinnamates **9** from the corresponding acetylenes **7** as shown in eq 3. Thus, phenyltellurenylation of **7** occurred regio- and stereoselectively (trans addition) to give completely (*Z*)-vinyl telluride (**8**) almost quantitatively, methoxycarbonylation of which proceeded with complete retention of configuration to

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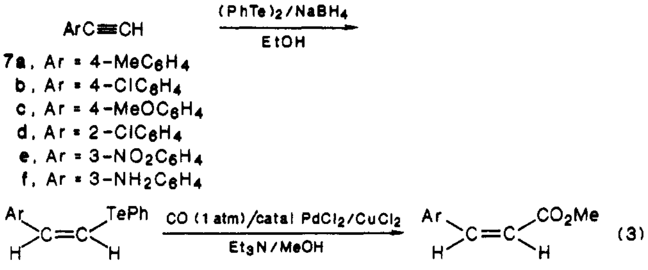
[4] Kasahara, A.; Izumi, T.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1639.

[5] The addition is completely trans. Separation of **5** from its regioisomer **5′** is facile by column chromatography on SiO_2. See: References 3c and 3f.

[6] (a) Larock, R. C. *J. Org. Chem.* **1975**, *40*, 3237. (b) Larock, R. C.; Riefling, B. *Tetrahedron Lett.* **1976**, 4661. (c) Larock, R. C.; Riefling, B.; Fellows, C. A. *J. Org. Chem.* **1978**, *43*, 131.

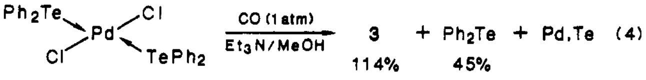
[7] Cowell, A.; Stille, J. K. *Tetrahedron Lett.* **1979**, *133*; *J. Am. Chem. Soc.* **1980**, *102*, 4193.



8 **9**

afford **9**. The results are also shown in Table II. In the case of (3-nitrophenyl)acetylene (**7e**), reduction of a nitro group to an amino group occurred during the tellurenylation procedure, and the product was 3-aminostyryl phenyl telluride (**8f**) in 60% yield. Such reduction by the $(PhTe)_2/NaBH_4$ system has been known.[8] The attempted methoxycarbonylation of **8f** resulted in formation of a complex mixture of unidentified compounds.

In a previous paper[2] we clarified that this type of carbonylation proceeded via monomeric and/or dimeric palladium complexes with organic tellurides.[9] Under the present reaction conditions this is also true, and actually both monomeric and dimeric complexes (**10** and **11**) were revealed to be more reactive. Thus, although in acetonitrile **10** did not react with CO and **11** afforded only 53% of **3**,[2] the treatment of either **10** or **11** with CO (1 atm) in methanol in the presence Et_3N afforded methyl benzoate (**3**) almost quantitatively together with liberated diphenyl telluride and a black solid (eq 4 and 5). The solid was almost IR inactive and scarcely contained C, H, and N, the metal analysis of which by inductively coupled plasma emission spectroscopy (ICPES) revealed it to mainly consist of palladium and tellurium. However, it is not yet clear whether this is a mixture of Pd and Te or a PdTe alloy. The black precipitate obtained from the reaction of **1a** in eq 1 was nearly the same in nature.



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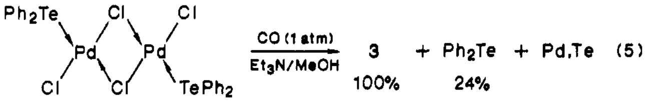


11

The present carbonylation by use of a stoichiometric amount of $PdCl_2$ seems to proceed via several steps shown in Scheme I with **1f** as a substrate. Namely, after the formation of complex **11** phenyl migration occurs to give phenylpalladium and phenyltellurium species (transmetalation; step i), and the former reacts with CO and methanol to give methyl benzoate and elemental palladium (carbonylation; step ii). The phenyltellurium species adds oxidatively to the palladium thus formed to give PhTePdCl, which might give PhPdCl and elemental tellurium (step iii). The species PhTePdCl may further react with Pd to afford PhPdTePdCl from which elimination of TePd occurs in the form of alloys or mixtures of each element as black precipitates leaving PhPdCl (step iv) followed by its carbonylation (step v = step ii). The assumption of the insertion of palladium to the Te–Cl bond (step iii) and to the C–Te bond (step iv) has a precedent in the reaction of aryltellurium trichlorides with nickel tetracarbonyl,[10] where nickel insertion to those bonds is proposed. On the other hand, in the catalytic reaction elemental palladium is oxidized readily to palladium(II), and so both steps iii and iv are inhibited. Instead, phenyltellurium species produced by step i may be captured by triethylamine as a form of $PhTeCl-Et_3N$ complex though we have not yet succeeded in identification of the complex. These assumptions are consistent with the facts that no black precipitate deposited and **3** was scarcely formed in the catalytic reaction of **1a**–**1e**. Further, in the cases of alkenyl and alkynyl phenyl tellurides, the transfer of alkenyl and alkynyl groups from Te to Pd is faster than that of the phenyl group as seen from the results in Table I, and thus the phenyltellurenyl group is captured in the form of the above described complex in the catalytic reaction, while in the stoichiometric reaction with enough $PdCl_2$ there may be a chance of phenyl group transfer to give PhPdCl, which affords **3**. We propose the catalytic cycle of this carbonylation as shown in Scheme II with $CuCl_2$ as a reoxidant. Other positive effects of Et_3N seem to be (1) the activation of the complexes **10** and **11** by changing them to new monomeric species having Et_3N as a ligand in which organic group transfer may be accelerated and (2) the capture of HCl from HPdCl for the rapid formation of elemental palladium.

Scheme I

$$PhTePh + PdCl_2 \rightarrow 11 \rightarrow PhPdCl + PhTeCl \qquad (i)$$

$$PhPdCl + CO + MeOH \rightarrow PhCO_2Me + Pd + HCl \qquad (ii)$$

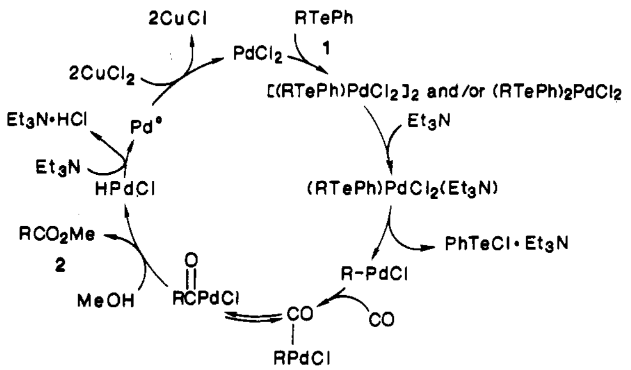
$$PhTeCl + Pd \rightarrow PhTePdCl\ (\rightarrow PhPdCl + Te) \qquad (iii)$$

$$PhTePdCl + Pd \rightarrow PhPdTePdCl \rightarrow PhPdCl + Pd,Te \qquad (iv)$$

$$PhPdCl + CO + MeOH \rightarrow PhCO_2Me + Pd + HCl \qquad (v)$$

$$PhTePh + PdCl_2 + 2CO + 2MeOH \rightarrow 2PhCO_2Me + 2HCl + Pd,Te$$

Scheme II



In order to know whether the corresponding sulfur and selenium compounds can be carbonylated under the present $CO/PdCl_2/Et_3N/MeOH$ system, the reactivities of diphenyl sulfide, (*Z*)-styryl phenyl sulfide, diphenyl selenide, and (*Z*)- and (*E*)-styryl phenyl selenides were examined. From organic sulfides, no methyl carboxylate and other carbonylation products were obtained, all starting materials being recovered intact. On the other hand, organic selenides afforded carbonylation products in improved yields compared with the previous $CO/PdCl_2/MeCN$ system (0–4%).[2] Thus, under the conditions shown in Table I (25 °C, 5 h), diphenyl selenide gave **3** in

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[8] Ohira, N.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1984**, 853.

[9] For organic telluride–palladium(II) complexes, see for example: Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 163; *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, 1986; Vol. 1, Chapter 18, p 679.

[10] Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *175*, 233.

16% yield, while (*Z*)- and (*E*)-styryl phenyl selenides afforded **2a** and **2b** (16%; **2a**/**2b** = 83/17) and **3** (10%), and **2b** (22%) and **3** (9%), respectively. Elongation of the reaction time or elevation of the reaction temperature did not improve the product yields.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on Hitachi Perkin-Elmer R-600 (60-MHz), JEOL JNM FX-100 (100-MHz), and JEOLCO GX-400 (400-MHz) spectrometers as solutions in $CDCl_3$. ^{13}C NMR spectra were determined on a Fourier transform NMR system (JNM FX-100) in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. The coupling constants (J) are in hertz (Hz). IR spectra were recorded on Perkin-Elmer 521 and Jasco IR-810 infrared spectrophotometers as KBr pellets (for solids) or thin films (for liquids). Inductively coupled plasma emission spectroscopy (ICPES) for determination of metal concentration was carried out on Nippon Jarrell-Ash ICPES, Model ICAP-500. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses (1 m × 0.5 cm columns packed with 5% silicone DC QF-1, 25% PEG 6000, and 3% EGSS-X, on Chromosorb W 60–80 mesh) were performed on a Yanaco G 2800 instrument with flame-ionization detectors and N_2 as carrier gas. All column chromatographies were performed with Wakogel C-200 (100–200 mesh). For preparative chromatography, plates precoated with Merck silica gel 60 F_{254} of 2-mm thickness were used.

Materials. Solvents were freshly distilled prior to use: methanol was distilled from magnesium methoxide prepared in situ from magnesium, iodine, and methanol; methylene chloride was distilled from calcium hydride. Diphenyl ditelluride was prepared by the reported method.[11] The following known organotellurium, -selenium, and -sulfur compounds were prepared by reported methods: (Z)-$PhCH{=}CHTePh$ (**1a**),[3c] (E)-$PhCH{=}CHTePh$ (**1b**),[2] (Z)-$EtO_2CCH{=}CHTePh$ (**1c**),[3c] $PhC{\equiv}CTePh$ (**1d**),[11] n-$C_{12}H_{25}TePh$ (**1g**),[12] $(p\text{-}MeOC_6H_4)_2TeCl_2$,[13] $(p\text{-}MeOC_6H_4)_2Te$,[14] (Z)-$PhCH{=}CHSePh$,[15] (E)-$PhCH{=}CHSePh$,[16] (Z)-$PhCH{=}CHSPh$,[17] 3-hydroxy-1-alkenyl phenyl tellurides **5a**–**5d**.[3c,3f] The compounds **1e** and **5e** are new. **1e**: prepared in 85% yield by modifying the literature method[11] with n-BuLi in place of EtMgBr; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.89 (t, 3 H, 1.08–1.72 (m, 8 H), 2.56 (t, J = 6.9 Hz, 2 H), 7.08–7.28 (m, 3 H), 7.54–7.72 (m, 2 H). Anal. Calcd for $C_{14}H_{18}Te$: C, 53.57; H, 5.78. Found: C, 53.42; H, 5.58. **5e**: prepared as a mixture with a minor amount of $CH_3CH(OH)C(TePh){=}CH_2$ (84/16 by GLC) by the reported method[5] and separated in a pure form by column chromatography on SiO_2 (60% yield); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.18 (s, 1 H), 1.31 (d, J = 6.4 Hz, 3 H), 4.45 (m, 1 H), 6.41 (dd, J = 9.7, 5.6 Hz, 1 H), 6.84 (dd, J = 9.7, 1.3 Hz, 1 H), 7.15–7.30 (m, 3 H), 7.70–7.75 (m, 2 H). Anal. Calcd for $C_{10}H_{20}OTe$: C, 43,55; H, 4.39. Found: C, 43.11; H, 4.36. Commercial diphenyl telluride (**1f**), diphenyl selenide, and diphenyl sulfide were used without further purification. Various ring-substituted phenylacetylenes **7a**–**7e** were prepared by literature procedures.[18] Transition-metal salts such as $PdCl_2$, $Pd(OAc)_2$, $RuCl_3$, $RhCl_3{\cdot}3H_2O$, $IrCl_3$, $CuCl_2$, CuCl, and $FeCl_3$ as well as $Ce(NH_4)_2(NO_3)_6$ and p-benzoquinone were commercial products. Bis(diphenyl telluride)dichloropalladium (**10**) and bis(diphenyl telluride)dichlorobis(μ-chloro)palladium (**11**) were synthesized as reported previously.[2]

Preparation of (*Z*)-$ArCH{=}CHTePh$ (8). In a 50-mL round-bottom flask containing a magnetic stirring bar were placed diphenyl ditelluride (1.02 g, 2.5 mmol) and $NaBH_4$ (0.24 g, 6.3 mmol) under nitrogen. Ethanol (10 mL) was added to the flask at 0 °C, and the mixture became homogeneous after being stirred for 0.5 h at room temperature, during which the color of the solution turned from orange to pale yellow. An ethanol (5 mL) solution of arylacetylene (**7**, 5.0 mmol) was then added to the resulting solution, and the mixture was stirred at reflux for 20 h. After it had been cooled, the mixture was treated with brine and then extracted with $CHCl_3$ (3 × 50 mL), and the extract was dried over $MgSO_4$. Evaporation of $CHCl_3$ left a crude product, which was subjected to column chromatography on silica gel or recrystallized from ethanol.

(*Z*)-4-Methylstyryl Phenyl Telluride (8a). Recrystallization of an orange crude solid (1.56 g, 97% yield) from ethanol afforded a yellow solid of pure **8a**: 74% yield; mp 54.5–55.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3 H), 7.03 (d, J = 10.5 Hz, 1 H), 7.14 (d, J = 8.1 Hz, 2 H), 7.21 (d, J = 8.1 Hz, 2 H), 7.22–7.35 (m, 3 H), 7.45 (d, J = 10.5 Hz, 1 H), 7.76–7.80 (m, 2 H). Anal. Calcd for $C_{15}H_{14}Te$: C, 55.97; H, 4.38. Found: C, 55.98; H, 4.47.

(*Z*)-4-Chlorostyryl Phenyl Telluride (8b). Recrystallization of a yellow crude solid (1.70 g, 99% yield) afforded a yellow solid of pure **8b**: 86% yield; mp 72.5–74.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 10.8 Hz, 1 H), 7.17 (d, J = 8.3 Hz, 2 H), 7.35 (d, J = 8.3 Hz, 2 H), 7.24–7.38 (m, 3 H), 7.41 (d, J = 10.8 Hz, 1 H), 7.75–7.80 (m, 2 H); ^{13}C NMR (25.1 MHz, $CDCl_3$) δ 110.0 (d, $PhTe\mathit{C}{=}$), 115.0 (s, PhTe, C(1)), 128.3 (d, $4\text{-}ClC_6H_4$, C(2)), 128.7 (d, PhTe, C(4)); (d, $4\text{-}ClC_6H_4$, C(3)), 129.5 (d, PhTe, C(3)), 133.3 (s, $4\text{-}ClC_6H_4$, C(4)), 135.9 (d, $4\text{-}ClC_6H_4C{=}$), 137.5 (s, $4\text{-}ClC_6H_4$, C(1)), 138.1 (d, PhTe, C(2)). Anal. Calcd for $C_{14}H_{11}ClTe$: C, 49.13; H, 3.24. Found: C, 49.12; H, 3.35.

(*Z*)-4-Methoxystyryl Phenyl Telluride (8c). Recrystallization of a dark orange crude solid (1.74 g, 88% yield) afforded a yellow solid of pure **8c**: 72% yield; mp 60.5–62.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3 H), 6.93 (d, J = 8.8 Hz, 2 H), 6.95 (d, J = 10.3 Hz, 1 H), 7.19 (d, J = 8.8 Hz, 2 H), 7.25–7.35 (m, 3 H), 7.42 (d, J = 10.3 Hz, 1 H), 7.76–7.79 (m, 2 H). Anal. Calcd for $C_{15}H_{14}OTe$: C, 53.32; H, 4.18. Found: C, 53.05; H, 4.18.

(*Z*)-2-Chlorostyryl Phenyl Telluride (8d). Column chromatography on SiO_2 (hexane as eluent) afforded a yellow oil of **8d**: 1.63 g, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.41 (m, 7 H), 7.23 (d, J = 10.3 Hz, 1 H), 7.59 (d, J = 10.3 Hz, 1 H), 7.74–7.79 (m, 2 H). Anal. Calcd for $C_{14}H_{11}ClTe$: C, 49.13; H, 3.24. Found: C, 49.53; H, 3.27.

(*Z*)-3-Aminostyryl Phenyl Telluride (8f). An ethanol (5 mL) solution of (3-nitrophenyl)acetylene (0.749 g, 5.0 mmol) was added to an ethanol solution of diphenyl ditelluride (1.02 g, 2.5 mmol) and $NaBH_4$ (0.24 g, 6.3 mmol) at 0 °C, and the resulting dark red solution was stirred at room temperature for 1 h, during which orange precipitates deposited. An ethanol (15 mL) suspension of $NaBH_4$ (0.38 g, 10.0 mmol) was further added to the above mixture at 0 °C, and then the resulting solution was stirred at reflux for 20 h. After it has been cooled down, the brown yellow mixture was treated as described above. Evaporation of $CHCl_3$ left an oily residue, which was subjected to column chromatography on SiO_2 [hexane/ethyl acetate (1:1) as eluent] to give an orange oil of **8f**: 0.97 g, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (br s, 2 H), 7.02 (d, J = 10.5 Hz, 1 H), 7.13–7.32 (m, 7 H), 7.36 (d, J = 10.5 Hz, 1 H), 7.74–7.78 (m, 2 H); IR (neat) 3450, 3380, 3050, 1940, 1870, 1810, 1620, 1600, 1575, 1495, 1475, 1460, 1435, 1320, 1270, 1170, 1065, 1020, 1000, 875, 795, 730, 695 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NTe$: C, 52.08; H, 4.06; N, 4.34. Found: C, 52.79; H, 4.10; N, 4.38.

General Procedure for Methoxycarbonylation of Organic Tellurides by Use of Stoichiometric Pd(II) Salts. In a two-necked 50-mL round-bottom flask with a septum inlet and a three-way stopcock were placed palladium(II) chloride (0.177 g, 1.0 mmol) and a telluride (1.0 mmol). The system was then flushed with CO from a CO balloon connected to the flask at 25 °C, to which dry methanol (10 mL) and triethylamine (0.202 g, 2.0 mmol) were added by a syringe. After the mixture was stirred

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[17] Prepared in 60% yield from phenylacetylene, diphenyl disulfide, and $NaBH_4$ in ethanol at reflux for 20 h: ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.45 (d, J = 10.7 Hz, 1 H), 6.58 (d, J = 10.7 Hz, 1 H), 7.1–7.5 (m, 10 H). By standing at room temperature this (Z) isomer isomerized partly to the (E) isomer. The (Z) isomer is the known compound: Oswald, A. A.; Griesbaum, K.; Hudson, B. E., Jr.; Bregman, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 2877.

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for 5 h at 25 °C, a precipitated black solid was filtered off. The filtrate was poured into NH_4Cl aqueous solution and extracted with diethyl ether (3 × 30 mL). The products were determined by GLC using an EGSS-X 3% (1-m) column.

The black solid obtained from carbonylation of **1a** (0.308 g, 1.0 mmol) was washed with $CHCl_3$ and then diethyl ether and dried in vacuo (0.236 g). This was almost IR inactive and scarcely contained C, H, and N by combustion analysis. ICPES of the solid revealed the presence of tellurium (52.0%) at 238.578 nm and palladium (41.0%) at 363.4695 nm.

General Procedure for $PdCl_2$-Catalyzed Methoxycarbonylation of Organic Tellurides with Carbon Monoxide. In a two-necked 50-mL round-bottom flask with a septum inlet and a three-way stopcock were placed palladium(II) chloride (0.017 g, 0.1 mmol), copper(II) chloride (0.270 g, 2.0 mmol), and a telluride (1.0 mmol). The system was then flushed with CO from a CO balloon connected to the flask at 25 °C, to which dry methanol (10 mL) and triethylamine (0.303 g, 3.0 mmol) were added by a syringe. After the mixture was stirred for 75 h at 25 °C, during which the green color turned to dark brown, the brown solid was filtered off. The filtrate was poured into NH_4Cl aqueous solution and extracted with diethyl ether (3 × 30 mL). Products were isolated by preparative TLC or Kugelrohr distillation or determined by GLC using an EGSS-X 3% (1-m) column with an appropriate internal standard.

(*Z*)-Methyl 3-(4-Methylphenyl)propenoate (9a).[19] Treatment of **8a** (1.0 mmol) with CO under catalytic conditions afforded **9a**, which was isolated by preparative TLC eluted with hexane/EtOAc (10:1) as a pale yellow liquid: 0.105 g, 0.596 mmol, 59.6% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 3.71 (s, 3 H), 5.89 (d, J = 13 Hz, 1 H), 6.92 (d, J = 13 Hz, 1 H), 7.15 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H); IR (neat) 1720 (s), 1625, 1610, 1515, 1440, 1200, 1170 (s), 1000, 840 cm^{-1}.

(*Z*)-Methyl 3-(4-Chlorophenyl)propenoate (9b).[19] Kugelrohr distillation [bp 185–190 °C (2 mmHg)] gave 0.144 g (72.5% yield) of **9b** as a colorless liquid: ^1H NMR (60 MHz, $CDCl_3$) δ 3.72 s, 3 H), 5.96 (d, J = 13 Hz, 1 H), 6.91 (d, J = 13 Hz, 1 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H); IR (neat) 1725 (s), 1630, 1495, 1200 (s), 1170 (s), 1095, 845 cm^{-1}.

(*Z*)-Methyl 3-(4-Methoxyphenyl)propenoate (9c).[19] Kugelrohr distillation [bp 202–210 °C (1 mmHg)] gave 0.137 g (71.3% yield) of **9c** as a colorless liquid: ^1H NMR (60 MHz, $CDCl_3$) δ 3.73 (s, 3 H), 3.82 (s, 3 H), 5.83 (d, J = 13 Hz, 1 H), 6.87 (d, J = 13 Hz, 1 H), 6.88 (d, J = 8.4 Hz, 2 H), 7.70 (d, J = 8.4 Hz, 2 H); IR (neat) 3000, 2950, 2850, 1725 (s), 1625, 1605 (s), 1510 (s), 1445, 1260 (s), 1220 (s), 1170 (s), 1035, 845 cm^{-1}.

(*Z*)-Methyl 3-(2-Chlorophenyl)propenoate (9d). Kugelrohr distillation [bp 160–170 °C (2 mmHg)] gave 0.157 g (79.8% yield) of **9d** as a colorless liquid: ^1H NMR (100 MHz, $CDCl_3$) δ 3.65 (s, 3 H), 6.08 (d, J = 12 Hz, 1 H), 7.15 (d, J = 12 Hz, 1 H), 7.18–7.55 (m, 4 H); IR (neat) 1725 (s), 1635 (s), 1440 (s), 1270, 1200 (s), 1170 (s), 1050, 1035, 825 (s), 760 (s) cm^{-1}. Anal. Calcd for $C_{10}H_9ClO_2$: C, 61.08; H, 4.61. Found: C, 61.07; H, 4.60.

$PdCl_2$-Catalyzed Carbonylation of 3-Hydroxy-1-alkenyl Phenyl Telluride (5). $\Delta^{\alpha,\beta}$-Butenolides were prepared according to the following representative procedure. Palladium(II) chloride (0.018 g, 0.1 mmol) and copper (II) chloride (0.270 g, 2.0 mmol) were placed in a round-bottom flask with a septum inlet. After the mixture was flushed with carbon monoxide from a CO balloon connected to the flask, dry CH_2Cl_2 (5 mL), a CH_2Cl_2 (5 mL) solution of an appropriate telluride (1.0 mmol), and triethylamine (0.303 g, 3.0 mmol) were added successively at 5 °C. The resulting mixture was stirred for 75 h at 5 °C and then filtered from a brown precipitate. A filtrate was washed with 0.5 N NaOH aqueous solution and then with saturated ammonium chloride solution and dried over $MgSO_4$. GLC analysis of the filtrate revealed the presence of the corresponding $\Delta^{\alpha,\beta}$-butenolides **6b** and **6c**. For isolation of the butenolide the reaction using stoichiometric $PdCl_2$ (1 mmol) was carried out at 5 °C for 20 h, and the product was distilled (Kugelrohr) under reduced pressure. The isolated yields and the characterization of **6a–6c** are as follows.

5,5-Dimethyl-2(5*H*)-furanone (6a): 22%; bp 80–90 °C (10 mmHg) [lit.[20] bp 85–88 °C (10 mmHg)]; ^1H NMR (100 MHz, $CDCl_3$) δ 1.50 (s, 6 H), 5.99 (d, J = 6 Hz, 1 H), 7.44 (d, J = 6 Hz, 1 H); IR (ν_{max}, neat) 1750 (C=O) cm^{-1}.

5,5-Pentamethylene-2(5*H*)-furanone (6b): 51%; bp 200–205 °C (1 mmHg); ^1H NMR (60 MHz, $CDCl_3$) δ 1.68 (s, 10 H), 6.01 (d, J = 6 Hz, 1 H), 7.48 (d, J = 6 Hz, 1 H); IR (ν_{max}, neat) 1750 (C=O) cm^{-1}. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.45; H, 7.25.

5-Isobutyl-5-methyl-2(5*H*)-furanone (6c): 43%; bp 185–190 °C (1 mmHg); ^1H NMR (60 MHz, $CDCl_3$) δ 0.92 (d, J = 6 Hz, 6 H), 1.10–1.40 (m, 1 H), 1.45 (s, 3 H), 1.69 (t, 2 *H*), 6.01 (d, J = 6 Hz, 1 H), 7.40 (d, J = 6 Hz, 1 H); IR (ν_{max}, neat) 1750 (C=O) cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.94; H, 8.75.

Treatment of Complexes 10 and 11 with Carbon Monoxide. A balloon filled with CO was connected to a round-bottom flask with a septum inlet in which the complex $[(Ph_2Te)PdCl_2]_2$ (**11**; 0.46 g, 0.5 mmol) was placed, and the system was flushed with CO. Dry methanol (10 mL) and triethylamine (0.204 g, 2.0 mmol) were then added by a syringe, and the mixture was stirred for 5 h at 25 °C. A black precipitate formed (0.180 g; IR inactive; Te 43.9%, Pd 48.2% by ICPES) was filtered and washed with diethyl ether (100 mL). The ether layer was washed with saturated ammonium chloride solution and dried over $MgSO_4$. GLC analysis of the extract revealed the presence of methyl benzoate (1.04 mmol) and the dissociated diphenyl telluride (0.24 mmol).

The reaction of the complex $(Ph_2Te)_2PdCl_2$ (**10**; 0.38 g, 0.5 mmol) with CO was similarly carried out in methanol (5 mL) in the presence of triethylamine (0.202 g, 2.0 mmol). GLC analysis revealed the presence of methyl benzoate (0.57 mmol) and the dissociated diphenyl telluride (0.45 mmol). A black solid formed (0.087 g) was also IR inactive and contained Te (46.0%) and Pd (38.3%).

Coupling Reaction of 1d. To a round-bottom flask (50 mL) was added copper(II) chloride (0.122 g, 0.9 mmol), and then the system was flushed with CO from a CO balloon connected to the flask at 25 °C to which dry methanol (3 mL), a methanol (2 mL) solution of **1d** (0.131 g, 0.43 mmol), and triethylamine (0.101 g, 1.0 mmol) were added by a syringe. After the mixture was stirred for 20 h at 25 °C, a precipitated green solid was filtered off. The organic layer was poured into NH_4Cl aqueous solution and extracted with diethyl ether (3 × 20 mL). GLC analysis of the extract revealed the presence of 1,4-diphenyl-1,3-butadiyne (0.17 mmol, 79% yield).

On the other hand, the reaction of **1d** (0.153 g, 0.5 mmol) with copper(I) chloride (0.10 g, 1.0 mmol) under similar conditions did not produce any 1,4-diphenyl-1,3-butadiyne, the **1d** remaining was 39% (by GLC).

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Registry No. **1a**, 82296-87-5; **1b**, 110295-96-0; **1c**, 82296-85-3; **1d**, 56950-09-5; **1e**, 110296-07-6; **1f**, 1202-36-4; **1g**, 75250-42-9; **2a**, 19713-73-6; **2b**, 1754-62-7; **2c**, 19896-44-7; **2d**, 4891-38-7; **2e**, 111-80-8; **2f**, 121-98-2; **2g**, 1731-88-0; **3**, 93-58-3; **3** (acid), 65-85-0; **5a**, 110295-97-1; **5b**, 110295-98-2; **5c**, 110295-99-3; **5d**, 82296-86-4; **5e**, 110296-00-9; **6a**, 20019-64-1; **6b**, 4435-19-2; **6c**, 110296-01-0; **7a**, 766-97-2; **7b**, 873-73-4; **7c**, 768-60-5; **7d**, 873-31-4; **7f**, 54060-30-9; **8a**, 110296-03-2; **8b**, 110296-04-3; **8c**, 110296-05-4; **8d**, 110296-06-5; **8f**, 110296-08-7; **9a**, 50363-84-3; **9b**, 20754-24-9; **9c**, 19310-29-3; **9d**, 110296-02-1; $(4\text{-}MeOC_6H_4)_2Te$, 4456-34-2; $(4\text{-}MeOC_6H_4)_2TeCl_2$, 4456-36-4; $(PhC{\equiv}C)_2$, 886-66-8; $(C_6H_{13}C{\equiv}C)_2$, 18277-20-8; $C_{12}H_{26}$, 112-41-4.

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