312 *Organometallics* **2010,** *29,* 312–316
DOI: 10.1021/om9008982

ORGANOMETALLICS
Article

Highly Selective Phosphinotelluration of Terminal Alkynes Using a $(Ph_2P)_2-(PhTe)_2$ Mixed System upon Visible Light Irradiation: Straightforward Access to 1-Phosphino-2-telluro-alkenes

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Received October 13, 2009

Simultaneous and regioselective introduction of both phosphino and telluro groups into carbon−carbon triple bonds has been attained successfully by using a novel mixed system of diphosphine and ditelluride under visible light irradiation conditions. Upon irradiation with a xenon lamp (500 W) through the filter ($h\nu > 400$ nm), terminal alkynes undergo highly selective phosphinotelluration in the presence of tetraphenyldiphosphine and diphenyl ditelluride, affording 1-(diphenylphosphino)-2-(phenyltelluro)alkenes, regioselectively, in moderate to good yields. The regioselectivity of this phosphinotelluration of terminal alkynes is discussed by comparison with those of the thiophosphination using a $(Ph_2P)_2-(PhS)_2$ binary system and the selenophosphination using a $(Ph_2P)_2-(PhSe)_2$ binary system.

Introduction

Simultaneous introduction of two different heteroatom groups into carbon−carbon unsaturated bonds is a powerful tool to give multifunctionalized organic compounds directly. For this purpose, radical addition reactions of interelement compounds into unsaturated bonds via homolytic cleavage of heteroatom−heteroatom linkages are promising, because the combination of interelement compounds makes it possible to synthesize a wide variety of multifunctionalized heteroatom compounds.[1,2] Along this line, we have recently developed simultaneous and selective introduction of two different heteroatom groups to carbon−carbon unsaturated bonds using novel mixed systems of interelement compounds under photoirradiation conditions. In the case of the addition to alkynes, for example, we already reported highly selective thioselenation, thiotelluration, selenotelluration, thiophosphination, and selenophosphination using $(PhS)_2-(PhSe)_2$,[3] $(PhS)_2-(PhTe)_2$,[4] $(PhSe)_2-(PhTe)_2$,[4b] $(PhS)_2-(Ph_2P)_2$,[5] and $(PhSe)_2-(Ph_2P)_2$[6] mixed systems, respectively, as shown in Scheme 1.

These interelement compounds (Y−Y, Z−Z) undergo homolytic cleavage upon photoirradiation, generating the corresponding heteroatom-centered radicals (Y•, Z•), respectively.[7−10]

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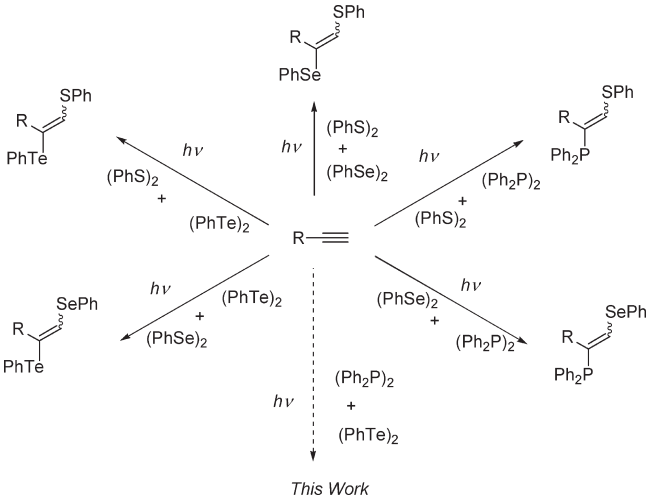
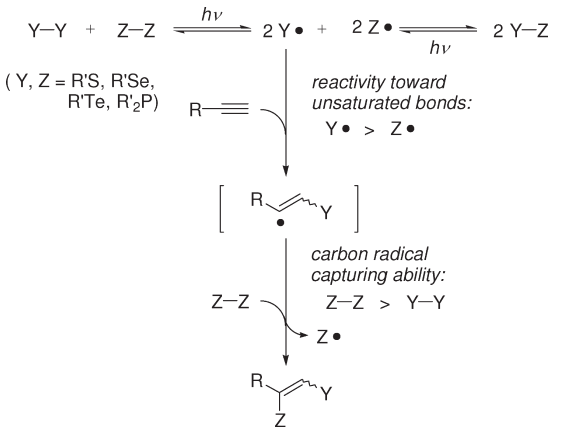
 Published on Web 12/16/2009

Scheme 1. Simultaneous Introduction of Two Different Heteroatom Groups Including PhS, PhSe, PhTe, or Ph_2P to Alkynes upon Photoirradiation



Scheme 2. Simultaneous Introduction of Two Different Heteroatom Groups Using Heteroatom Mixed Systems



Then these radicals react with carbon−carbon triple bonds, giving the corresponding adducts (Scheme 2).

The selectivity of these reactions is controlled by the relative reactivities of interelement compounds: If Y• is more reactive toward alkynes compared with Z•, alkynes undergo selective addition of Y•, generating the corresponding vinyl radical. Then, when Z−Z has higher carbon-radical-capturing ability compared with Y−Y, the formed vinyl radicals are captured selectively with Z−Z, affording the desired multifunctionalized vinyl compounds successfully. In this paper, we wish to report a novel simultaneous introduction of both phosphino and telluro groups into alkynes upon photoirradiation using a $(Ph_2P)_2$−$(PhTe)_2$ mixed system.

Results and Discussion

When a mixture of 1-ethynyl-4-(trifluoromethyl)benzene (**1a**, 0.5 mmol), tetraphenyldiphosphine (**2**, 0.5 mmol), and diphenyl ditelluride (**3**, 0.5 mmol) in $CDCl_3$ (0.6 mL, degassed) was irradiated through a filter with a xenon lamp ($h\nu$ > 400 nm) at room temperature for 10 h, the desired product (**4a**) bearing both phosphino and telluro groups was obtained successfully in 96% yield (eq 1). In the cases of the thiophosphination and selenophosphination of alkynes, a thio or seleno group was introduced into the terminal position of alkynes, and the phosphino group was introduced into the inner one, regioselectively.[5,6] Surprisingly, X-ray analysis of **5a** indicated different regioselectivity: a phosphino group and telluro group were introduced into the terminal and inner positions, respectively, with excellent regioselectivity (Figure 1). Then the subsequent oxidation under air for 24 h led to the corresponding phosphinyltellurostyrene derivative (**5a**) in 73% yield.

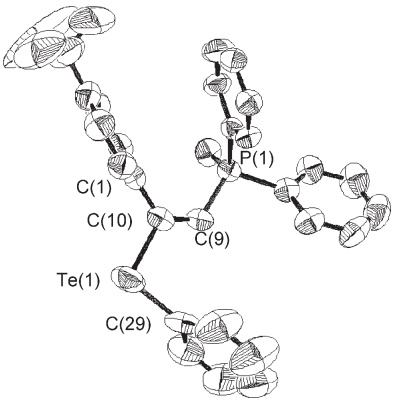
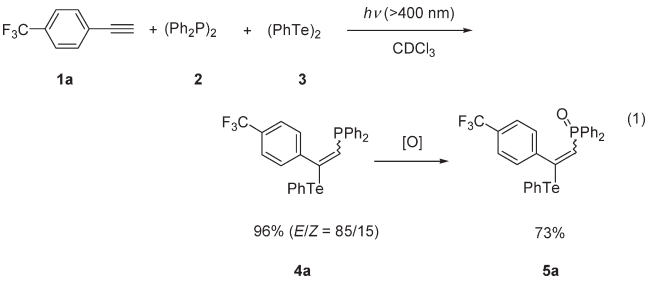


Figure 1. ORTEP drawing of **5a** depicted with thermal ellipsoids at 50% probability. The hydrogens have been omitted for clarity, and the CF_3 group is disordered. Selected bond distances (Å) and bond angles (deg): C(9)−C(10), 1.317(6); C(1)−C(10), 1.474(7); P(1)−C(9), 1.794(4); Te(1)−C(10), 2.125(4); Te(1)−C(29), 2.083(7); C(10)−Te(1)−C(29), 96.5(2); Te(1)−C(10)−C(9), 122.1(3); C(1)−C(10)−C(9), 125.1(4); P(1)−C(9)−C(10), 125.6(3).

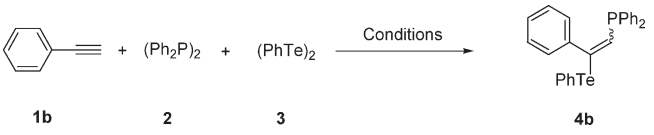


In these dichalcogenide−diphosphine mixed systems, both chalcogeno and phosphino radicals are generated in situ (Scheme 2). Therefore, both chalcogeno and phosphino radicals may attack the terminal position of alkynes. In fact, however, either heteroatom-centered radical selectively attacks the alkynes. On the basis of these regioselectivities in the thiophosphination, selenophosphination, and phosphinotelluration, the relative reactivity toward alkynes can be estimated as follows: PhS• > PhSe• > Ph_2P• > PhTe•.

Next, we examined this phosphinotelluration of phenylacetylene under several reaction conditions (Table 1). Without photoirradiation, the desired phosphinotelluration did not proceed at room temperature for a long time (entry 1). Even upon heating at 60 °C, the phosphinotelluration did not take place (entry 2). When irradiation through a filter with a xenon lamp ($h\nu$ > 400 nm) was conducted at room temperature for 10 h, the phosphinotelluration product (**4b**) was obtained in good yield (entry 3). In the case of benzene[11]

(11) Chloroform or benzene was used as a solvent because tetraphenyldiphosphine has lower solubility in other common organic solvents.[10c]

Table 1. Phosphinotelluration of Phenylacetylene under Several Conditions

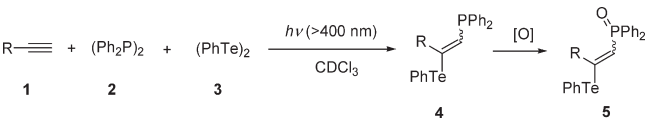


1b **2** **3** **4b**

entry	conditions (irradiation, temp, time, solvent)	yield[a]
1	dark, rt, 90 h, $CDCl_3$	trace
2	dark, heat (60 °C), 10 h, $CDCl_3$	trace
3	*hν* (>400 nm), rt, 10 h, $CDCl_3$	50%
4	*hν* (>400 nm), rt, 15 h, C_6D_6	trace

[a]Determined by ^{1}H NMR.

Table 2. Photoinduced Phosphinotelluration of Alkynes Using $(Ph_2P)_2$−$(PhTe)_2$ Mixed System



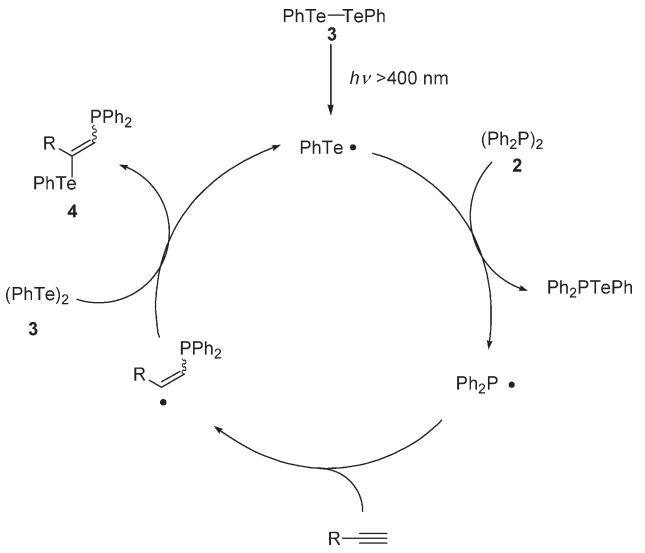
1 **2** **3** **4** **5**

entry	alkyne	time	product yield: **4** [*E*/*Z*][a]	**5** [*E*/*Z*]
1	F_3C **1a**	10 h	96% [85/15] **4a**	73%[b] *E*-**5a**
2	**1b**	10 h	50% [81/19] **4b**	40%[b] *E*-**5b**
3	MeO **1c**	14 h	74% [82/18] **4c**	52% [64/36][c] **5c**
4	Me **1d**	19 h	47% [81/19] **4d**	35% [71/29][c] **5d**
5	^{n}Pen **1e**	36 h	80% [76/24] **4e**	44% [79/21][c] **5e**
6	F **1f**	30 h	37% [80/20] **4f**	30% [77/23][c] **5f**
7	Br **1g**	30 h	45% [80/20] **4g**	23% [84/16][c] **5g**
8	**1h**	34 h	52% [23/77] **4h**	41% [7/93][c] **5h**
9	^{n}Hex **1i**	85 h	39% [82/18] **4i**	34% [75/25][c] **5i**

[a]Determined by ^{1}H and ^{31}P NMR. [b]Isolated yield of *E*-isomer by silica gel column chromatography. [c]Isolated yield of *E*/*Z* mixture. *E*/*Z* stereoisomer ratio determined by ^{1}H and ^{31}P NMR.

as solvent, the addition did not proceed (entry 4). Since the absorption maximum (λ_{max}) of diphosphine and ditelluride is 260 nm[12] and 406 nm,[9] respectively, visible-light irradiation induces selective cleavage of the ditelluride, generating PhTe•, which attacks the diphosphine to form Ph_2P• and $PhTePPh_2$.

Scheme 3. Possible Pathway for Phosphinotelluration of Alkynes



The phosphinotelluration of several alkynes was examined, and the results are shown in Table 2. A variety of aromatic alkynes successfully underwent regioselective phosphinotelluration in moderate to high yields (entries 1−7). In the case of a conjugate enyne, the phosphinotelluration proceeded in moderate yield (entry 8). The phosphinotelluration of aliphatic alkyne also proceeded regioselectively, although prolonged photoirradiation was required (entry 9). All of the obtained phosphinotelluroethenes **4a**−**i** could be transferred to the corresponding phosphine oxides **5a**−**i**.

A possible pathway for the present phosphinotelluration is shown in Scheme 3. As described already, the initiation for this phosphinotelluration can be explained by the visible-light-irradiated selective homolysis of ditelluride generating PhTe•. The formed PhTe• attacks $(Ph_2P)_2$ to form the phosphino radical (Ph_2P•) and $PhTePPh_2$, because the reactivity of PhTe• toward carbon−carbon triple bonds is relatively low. The formed Ph_2P• attacks the terminal carbon of alkynes, generating vinyl radical intermediate, which can be captured with $(PhTe)_2$ to give the phosphinotelluration products **4**, since $(PhTe)_2$ has a higher ability for capturing carbon radical compared with $(Ph_2P)_2$.

Conclusion

We have developed novel phosphinotelluration of terminal alkynes by the combination of $(Ph_2P)_2$ and $(PhTe)_2$ under photoirradiation conditions. This system has achieved simultaneous and regioselective introduction of both phosphino and telluro groups into carbon−carbon triple bonds. We are currently investigating the application of this system to the other compounds bearing heteroatom−heteroatom linkages.

Experimental Section

General Comments. Alkynes, tetraphenyldiphosphine (**2**), and diphenyl ditelluride (**3**) were obtained as commercial supplies. Alkynes were purified by distillation before use. Other materials

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were used without further purification. As the light source, USHIO optical ModuleX (SX-UI500XQ) was used. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP-500 (500 MHz) FT NMR system or JEOL JNM-400 (400 MHz) FT NMR system in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on a JEOL JNM-ECP-500 (125 MHz) FT NMR system or JEOL JNM-300SXA (75 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on a JEOL JNM- ECP-500 (200 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. The ^{125}Te NMR spectrum was taken on a JEOL JNM- ECP-500 (158 MHz) FT NMR system in $CDCl_3$. The chemical shift refers to $(PhTe)_2$ (δ = 420 ppm at 25 °C) in $CDCl_3$ as an external standard. IR spectra were determined on a Perkin-Elmer model 1600 spectrometer. Melting points were determined on a Yanagimoto micro melting point apparatus. HRMS were obtained on a JEOL JMS-DX303 in the analytical section of Osaka University. Elemental analyses were also performed there.

General Procedure for Photoinduced Phosphinotelluration of Alkynes with $(Ph_2P)_2$−$(PhTe)_2$ Mixed System. $(Ph_2P)_2$ (188 mg, 0.5 mmol), $(PhTe)_2$ (205 mg, 0.5 mmol), and alkyne (0.5 mmol) were placed in $CDCl_3$ (0.5 mL) in a sealed Pyrex glass NMR tube under a nitrogen atmosphere. The mixture was stirred for 30 s, and then the mixture was irradiated with a xenon lamp (500 W) though the filter ($h\nu > 400$ nm) at room temperature for 10−85 h. The reaction mixture was left under air for 24 h. Purification of the crude product was performed by preparative TLC. The *E* and *Z* mixture (**5c**−**5i**) was obtained with purification by preparative TLC to remove the starting materials and small amounts of byproduct. To separate the *E*- and *Z*-isomers of **5c**−**5i**, purification was performed by preparative TLC once more: for example **5c**, eluent AcOEt/hexane = 9:11, R_f = 0.15 for *E*-isomer, R_f = 0.32 for *Z*-isomer; **5d**, eluent AcOEt/hexane = 3:7, R_f = 0.10 for *E*-isomer, R_f = 0.15 for *Z*-isomer; **5e**, eluent AcOEt/hexane = 3:7, R_f = 0.10 for *E*-isomer, R_f = 0.23 for *Z*-isomer.

Spectral and Analytical Data. (*E*)-2-(Diphenylphosphinyl)-1-(phenyltelluro)-1-(4-trifluoromethylphenyl)ethene (*E*-5a): dark yellow solid; mp 64−66 °C; IR (NaCl) 3051, 1558, 1541, 1436, 1325, 1164, 1116, 746, 720, 694, 524 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.57 (d, J_{H-P} = 17.8 Hz, 1H), 7.21−7.35 (m, 12H), 7.40−7.44 (m, 5H), 7.87 (d, J = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.4, 124.5, 126.9 (q, J_{C-F} = 285.4 Hz), 128.1, 128.7, 129.6, 130.1, 130.4 (d, J_{C-P} = 90.0 Hz), 130.5 (q, J_{C-F} = 32.7 Hz), 130.7, 131.0, 131.2, 133.5 (d, J_{C-P} = 105.5 Hz), 141.0 (d, J_{C-P} = 1.9 Hz), 147.7 (d, J_{C-P} = 4.0 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.5; HRMS (EI) calcd for $C_{27}H_{20}F_3OPTe$ 578.0266, found 578.0260.

(*E*)-2-(Diphenylphosphinyl)-1-phenyl-1-(phenyltelluro)ethene (*E*-5b): dark yellow solid; mp 109−111 °C; IR (NaCl) 3051, 1558, 1541, 1436, 1184, 1114, 736, 719, 692, 520 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.45 (d, J_{H-P} = 17.9 Hz, 1H), 7.01−7.04 (m, 3H), 7.19−7.22 (m, 4H), 7.28−7.34 (m, 7H), 7.40−7.44 (m, 4H), 7.90−7.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 116.0, 126.1, 127.7, 127.9, 128.0 (d, J_{C-P} = 11.5 Hz), 128.6, 129.1 (d, J_{C-P} = 90.0 Hz), 130.0, 130.7 (d, J_{C-P} = 10.5 Hz), 130.9, 134.1 (d, J_{C-P} = 104.6 Hz), 139.8 (d, J_{C-P} = 8.6 Hz), 141.1, 150.5 (d, J_{C-P} = 4.8 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.4; ^{125}Te NMR (158 MHz, $CDCl_3$) δ 870; HRMS (EI) calcd for $C_{26}H_{21}OPTe$ 510.0392, found 510.0394. Anal. Calcd for $C_{26}H_{21}OPTe$: C, 61.47; H, 4.17. Found: C, 61.51; H, 4.18.

2-(Diphenylphosphinyl)-1-(4-methoxyphenyl)-1-(phenyltelluro)-ethene (5c): [*E*-isomer] yellow oil; IR (NaCl) 3054, 2924, 1541, 1435, 1175, 1119, 735, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.61 (s, 3H), 6.32 (d, J = 17.8 Hz, 1H), 6.48 (d, J_{H-P} = 8.7 Hz, 2H), 7.11−7.14 (m, 4H), 7.18−7.24 (m, 6H), 7.31−7.37 (m, 5H), 7.83 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.2, 113.2, 116.2, 125.7 (d, J_{C-P} = 91.9 Hz), 128.0 (d, J_{C-P} = 11.7 Hz), 128.5 (d, J_{C-P} = 13.6 Hz), 129.3, 129.7, 130.0, 130.6 (d, J_{C-P} = 9.2 Hz), 130.8 (d, J_{C-P} = 2.5 Hz), 132.8 (d, J_{C-P} = 105.5 Hz), 141.0, 150.3 (d, J_{C-P} = 52.4 Hz), 160.0; ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.6; HRMS (EI) calcd for $C_{27}H_{23}O_2PTe$ 540.0498, found 540.0500.

[*Z*-isomer] yellow oil; IR (NaCl) 3052, 2928, 1541, 1435, 1177, 1119, 735, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.66 (s, 3H), 6.53 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 6.9, 2H), 6.94 (d, J_{H-P} = 12.8 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 7.05−7.08 (m, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.47−7.50 (m, 4H), 7.52−7.56 (m, 2H), 7.69−7.82 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 112.8, 118.6, 122.8 (d, J_{C-P} = 95.5 Hz), 128.3 (d, J_{C-P} = 5.7 Hz), 128.4, 128.6 (d, J = 11.5 Hz), 129.4 (d, J_{C-P} = 7.8 Hz), 131.2 (d, J = 10.5 Hz), 131.8, 133.1 (d, J_{C-P} = 104.6 Hz), 135.7 (d, J_{C-P} = 19.1 Hz), 140.2 (d, J_{C-P} = 6.7 Hz), 152.2 (d, J_{C-P} = 1.9 Hz), 159.2; ^{31}P NMR (200 MHz, $CDCl_3$) δ 25.8; HRMS (EI) calcd for $C_{27}H_{23}O_2PTe$ 540.0498, found 540.0493.

2-(Diphenylphosphinyl)-1-(4-methylphenyl)-1-(phenyltelluro)-ethene (5d). [*E*-isomer] yellow oil; IR (NaCl) 3055, 2921, 2852, 2360, 1606, 1436, 1182, 1120, 794, 692, 524 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.10 (s, 3H), 6.30 (d, J_{H-P} = 18.1 Hz, 1H), 6.76 (d, J = 8.0 Hz, 2H), 7.09−7.16 (m, 6H), 7.19−7.24 (m, 4H), 7.71−7.76 (m, 5H), 7.84 (d, J = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 118.5, 123.0 (d, J_{C-P} = 106.5 Hz), 127.4, 127.8, 128.0, 128.3, 128.4 (d, J_{C-P} = 22.3 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 131.8, 133.1 (d, J_{C-P} = 104.1 Hz), 137.6, 140.3, 152.6; ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.8; HRMS (EI) calcd for $C_{27}H_{23}O_2PTe$ 524.0549, found 524.0553.

[*Z*-isomer] yellow oil; IR (NaCl) 3053, 2962, 2854, 2358, 1546, 1434, 1176, 1018, 792, 692, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.16 (s, 3H), 6.80 (d, J_{H-P} = 8.0 Hz, 2H), 6.88−6.90 (m, 5H), 7.07 (t, J = 7.3 Hz, 1H), 7.38 (d, J = 7.3 Hz, 2H), 7.48−7.55 (m, 6H), 7.78−7.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 118.4, 123.0 (d, J_{C-P} = 106.6 Hz), 127.4, 127.8, 128.0, 128.3, 128.6 (d, J_{C-P} = 11.6 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 131.8 (d, J_{C-P} = 2.5 Hz), 133.1 (d, J_{C-P} = 104.9 Hz), 137.5, 140.26, 140.33 (d, J_{C-P} = 13.2 Hz), 152.6; ^{31}P NMR (200 MHz, $CDCl_3$) δ 25.7; HRMS (EI) calcd for $C_{27}H_{23}O_2PTe$ 524.0549, found 524.0541.

2-(Diphenylphosphinyl)-1-(4-pentylphenyl)-1-(phenyltelluro)-ethene (5e): [*E*-isomer] yellow oil; IR (NaCl) 3053, 2928, 2856, 2172, 1437, 1303, 1184, 1117, 1101, 997, 736, 718, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.18−1.51 (m, 6H), 2.41 (t, J = 7.7 Hz, 2H), 6.40 (d, J_{H-P} = 17.6 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 7.14−7.52 (m, 15H), 7.91 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.4, 30.8, 31.3, 35.5, 116.2, 126.0 (d, J_{C-P} = 92.1 Hz), 127.8, 127.9 (d, J_{C-P} = 12.3 Hz), 128.7 (d, J_{C-P} = 21.5 Hz), 129.3, 130.0, 130.6, 130.8 (d, J_{C-P} = 9.9 Hz), 134.1 (d, J_{C-P} = 104.5 Hz), 137.1 (d, J_{C-P} = 8.2 Hz), 141.1, 143.7, 151.1; ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.6, HRMS (EI) calcd for $C_{31}H_{31}OPTe$ 580.1175, found 580.1176.

[*Z*-isomer] yellow oil; IR (NaCl) 3053, 2954, 2926, 2855, 2172, 1435, 1177, 1119, 1102, 997, 731, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, J = 7.2 Hz, 3H), 1.12−1.47 (m, 6H), 2.40 (t, J = 7.6 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 6.85−6.89 (m, 2H), 6.90 (d, J_{H-P} = 22.9 Hz, 1H), 6.93−6.97 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.46−7.55 (m, 6H), 7.76−7.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 31.02, 31.05, 35.3, 118.6, 122.6 (d, J_{C-P} = 105.3 Hz), 127.4, 127.8, 128.0, 128.2, 128.6 (d, J_{C-P} = 11.5 Hz), 131.2 (d, J_{C-P} = 9.9 Hz), 131.8 (d, J_{C-P} = 3.3 Hz), 133.1 (d, J_{C-P} = 108.6 Hz), 140.3, 140.4 (d, J_{C-P} = 20.6 Hz), 142.6, 152.7; ^{31}P NMR (200 MHz, $CDCl_3$) δ 25.7.

2-(Diphenylphosphinyl)-1-(4-fluorophenyl)-1-(phenyltelluro)-ethene (5f). [*E*-isomer] yellow oil; IR (NaCl) 3055, 2358, 2175, 1598, 1498, 1434, 1222, 1184, 1118, 1026, 792, 694, 559 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.50 (d, J_{H-P} = 18.3 Hz, 1H), 6.70 (t, $J_{H-F,H-H}$ = 8.8 Hz, 2 H), 7.22−7.26 (m, 3H), 7.29−7.33 (m, 4H), 7.40−7.45 (m, 6H), 7.81−7.84 (m, 2H), 7.88 (d, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.6 (d, J_{C-F} = 21.5 Hz), 127.4 (d, J_{C-P} = 91.7 Hz), 128.1 (d, J_{C-P} = 12.4 Hz), 128.5 (d, J_{C-F} = 13.2 Hz), 129.5, 130.1, 130.6 (d, J_{C-P} = 9.9 Hz),

131.0 (d, J_{C-P} = 2.5 Hz), 132.0 (d, J_{C-P} = 14.9 Hz), 133.9 (d, J_{C-P} = 104.9 Hz), 135.9 (dd, J_{C-P} = 8.3 Hz, J_{C-F} = 3.3 Hz), 141.0, 149.2, 162.6 (d, J_{C-F} = 248.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.9; HRMS (EI) calcd for $C_{26}H_{20}$FOPTe 528.0298, found 528.0290.

[*Z*-isomer] yellow oil; IR (NaCl) 3056, 2925, 2850, 1596, 1436, 1174, 1120, 729, 694, 559 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.66 (t, $J_{H-F,H-H}$ = 8.7 Hz, 2H), 6.88−6.94 (m, 3H), 6.98−7.00 (m, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 7.8 Hz, 2H), 7.45−7.50 (m, 4H), 7.53−7.56 (m, 2H), 7.77−7.81 (m, 4H); ^{31}P NMR (200 MHz, $CDCl_3$) δ 25.8; HRMS (EI) calcd for $C_{26}H_{20}$FOPTe 528.0298, found 528.0302.

1-(4-Bromophenyl)-2-(diphenylphosphinyl)-1-(phenyltelluro)-ethene (5g). [*E*-isomer] yellow oil; IR (NaCl) 3053, 2920, 2343, 1500, 1436, 1180, 1118, 798, 692, 524 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.49 (d, J_{H-P} = 18.0 Hz, 1H), 7.22−7.27 (m, 5H), 7.31−7.35 (m, 4H), 7.49−7.51 (m, 3H), 7.79−7.84 (m, 4H), 7.87−7.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.8, 127.6 (d, J_{C-P} = 99.0 Hz), 128.1 (d, J_{C-P} = 11.6 Hz), 128.7 (d, J_{C-P} = 14.0 Hz), 129.5, 129.6, 130.1, 130.65, 130.71 (d, J_{C-P} = 12.4 Hz), 131.1 (d, J_{C-P} = 2.5 Hz), 133.7 (d, J_{C-P} = 107.6 Hz), 138.8 (d, J_{C-P} = 9.1 Hz), 140.4, 141.0; ^{31}P NMR (200 MHz, $CDCl_3$) δ 18.0; HRMS (FAB) calcd for [M + H$^+$] $C_{26}H_{21}$BrOPTe 588.9576, found 588.9569.

[*Z*-isomer] yellow oil; IR (NaCl) 3053, 2962, 2360, 1546, 1475, 1434, 1174, 1120, 1068, 798, 692, 526 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.87 (d, J = 8.3 Hz, 2H), 6.91−6.94 (m, 2H), 7.08−7.12 (m, 4H), 7.39 (d, J = 6.9 Hz, 2H), 7.48−7.50 (m, 4H), 7.54−7.57 (m, 2H), 7.76−7.80 (m, 4H); ^{31}P NMR (200 MHz, $CDCl_3$) δ 26.0.

1-(1-Cyclohexenyl)-2-(diphenylphosphinyl)-1-(phenyltelluro)-ethene (5h): [*E*-isomer] yellow oil; IR (NaCl) 3445, 2168, 1645, 1603, 1501, 1437, 1290, 1252, 1177, 1115, 1026, 718, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91−1.09 (m, 4H), 1.62−1.99 (m, 4H), 6.03 (s, 1H), 6.66 (d, J_{H-P} = 19.6 Hz, 1H), 7.22−7.68 (m, 12H), 7.78−7.91 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 21.5, 25.0, 28.7, 114.7, 119.8, 125.6 (d, J_{C-P} = 96.5 Hz), 128.2 (d, J_{C-P} = 12.4 Hz), 129.0, 129.6, 130.9 (d, J_{C-P} = 9.2 Hz), 131.0 (d, J_{C-P} = 3.1 Hz), 134.8 (d, J_{C-P} = 103.8 Hz), 138.0 (d, J_{C-P} = 8.6 Hz), 141.0, 154.3; ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.6; HRMS (EI) calcd for $C_{26}H_{25}$OPTe 514.0705, found 514.0701.

[*Z*-isomer][13] pale yellow solid; mp 154−156 °C; IR (NaCl) 3412, 1645, 1603, 1504, 1435, 1250, 1173, 1115, 1026, 718, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92−0.96 (m, 2H), 1.04−1.07 (m, 2H), 1.67−1.69 (m, 2H), 1.78−1.79 (m, 2H), 5.47 (s, 1H), 6.69 (d, J = 28.4 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.20−7.23 (m, 1H), 7.37−7.41 (m, 4H), 7.44−7.47 (m, 2H), 7.64−7.71 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 21.6, 24.7, 29.4, 118.4, 119.5 (d, J_{C-P} = 105.5 Hz), 126.6, 127.9, 128.3, 128.5 (d, J_{C-P} = 12.4 Hz), 131.1 (d, J_{C-P} = 10.0 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 133.1 (d, J_{C-P} = 103.6 Hz), 141.1 (d, J_{C-P} = 18.5 Hz), 141.3, 156.3; ^{31}P NMR (200 MHz, $CDCl_3$) δ 25.9; HRMS (EI) calcd for $C_{26}H_{25}$OPTe 514.0705, found 514.0699. Anal. Calcd for $(C_{26}H_{25}OPTe)_{50}(CHCl_3)_1$: C, 59.99; H, 4.84. Found: C, 59.97; H, 4.74.

1-(Diphenylphosphinyl)-2-(phenyltelluro)oct-1-ene (5i): [*E*-isomer] brown oil; IR (NaCl) 3052, 2950, 2925, 2852, 1558, 1436, 1189, 726, 692, 497 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (t, J = 7.3 Hz, 3H), 1.00−1.12 (m, 6H), 1.32−1.38 (m, 2H), 2.78−2.82 (m, 2H), 6.12 (d, J = 23.3 Hz, 1H), 7.19−7.23 (m, 2H), 7.28−7.34 (m, 5H), 7.35−7.38 (m, 2H), 7.46−7.50 (m, 4H), 7.77−7.78 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0 22.4, 28.6, 30.6, 31.4, 38.8 (d, J_{C-P} = 7.6 Hz), 113.8, 124.6 (d, J_{C-P} = 92.1 Hz), 128.4 (d, J_{C-P} = 12.4 Hz), 129.1, 129.8, 130.7 (d, J_{C-P} = 9.5 Hz), 131.3, 134.6 (d, J_{C-P} = 103.6 Hz), 141.1, 155.0 (d, J_{C-P} = 3.8 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 19.7; HRMS (FAB) calcd for $C_{26}H_{29}$OPTe 518.1018, found 518.1020. Anal. Calcd for $C_{26}H_{29}$OPTe: C, 71.52; H, 6.69. Found: C, 71.76; H, 6.80.

[*Z*-isomer] brown oil; IR (NaCl) 3054, 2951, 2925, 2852, 1558, 1436, 1190, 726, 692, 500 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (t, J = 7.3 Hz, 3H), 0.90−0.97 (m, 4H), 1.04−1.11 (m, 2H), 1.26−1.33 (m, 2H), 2.20 (t, J = 7.3 Hz, 2H), 6.69 (d, J = 27.0 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 7.28−7.31 (m, 1H), 7.38−7.48 (m, 6H), 7.65−7.69 (m, 4H), 7.84 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.4, 28.3, 30.1, 31.4, 43.0 (d, J_{C-P} = 17.2 Hz), 116.2, 118.5 (d, J_{C-P} = 110.3 Hz), 128.6 (d, J_{C-P} = 10.5 Hz), 128.9, 130.9 (d, J_{C-P} = 10.5 Hz), 131.1 (d, J_{C-P} = 9.5 Hz), 131.7, 133.3 (d, J_{C-P} = 103.6 Hz), 142.0, 153.9; ^{31}P NMR (200 MHz, $CDCl_3$) δ 26.8.

Acknowledgment. This work is supported by a Grant-in-Aid for Scientific Research on Scientific Research (B, 19350095), from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and supported by a Grant-in-Aid for JSPS Fellows (No. 21-10516) from the Japan Society for the Promotion of Science.

Supporting Information Available: X-ray structure details for **5a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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