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Palladium- and copper-catalyzed cross-coupling and carbonylative cross-coupling of organotellurium compounds with organostannanes

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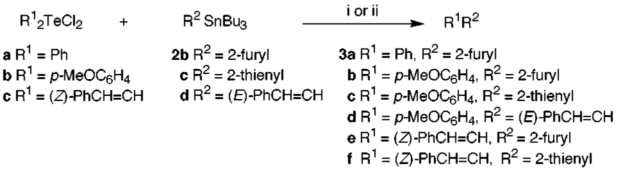
The palladium- and copper-catalyzed cross-coupling of diaryl- or divinyl tellurium dichlorides with organostannanes has been achieved in the presence of $PdCl_2$ (10 mol%) or CuI (10 mol%) with Cs_2CO_3 (2 equiv.) in MeCN in good to moderate yields; alternatively, the palladium- and copper-catalyzed carbonylative cross-coupling of organotellurium dichlorides with organostannanes was readily accomplished under atmospheric pressure of CO in good to moderate yields.

The palladium-catalyzed cross-coupling of organostannanes with an organic electrophile (*i.e.* halides and triflates), known as the Stille reaction,[1] has become an extremely powerful tool for the construction of carbon–carbon bonds. As alternatives to organic electrophiles, hypervalent iodonium salts[2] and the main group metal lead[3] have been employed in the cross-coupling with organostannaes. Recently Uemura *et al.* reported[4] the palladium-catalyzed carbonylation[4a] and homocoupling[4b] of vinyltellurides as well as the Heck type reaction[4c] of vinyltellurides. However the cross-coupling of aryl- or vinyltellurium dichlorides with organostannanes is not known. We assumed that the use of tellurium as one of the 6A group metals would expand the scope of the cross-coupling reaction. Here we report the palladium- and copper-catalyzed cross-coupling and carbonylative cross-coupling of diaryl- and divinyl-tellurium dichlorides[5] with organostannanes.

The results of Pd- and Cu-catalyzed cross-coupling and carbonylative cross-coupling of diaryl- or divinyl-tellurium dichlorides in MeCN at room temperature are summarized in Scheme 1 and Table 1. The palladium-catalyzed coupling of diphenyltellurium dichloride **1a** with 2-furyltributylstannane **2b** was carried out to find the optimum conditions. Of the catalysts tested [$PdCl_2$, $Pd(PPh_3)_4$, $Pd_2(dba)_3{\cdot}CHCl_3$, $PdCl_2(PPh_3)_2$], $PdCl_2$ was the best choice. Among the bases used, Cs_2CO_3 was more suitable than K_2CO_3, Na_2CO_3 and NaOMe. As solvent MeCN was the most preferable. In our hands, the cross-coupling of $PhTeCl_3$, p-$MeOC_6H_4TeCl_3$ and (*E*)-$PhCH{=}CHTeCl_3$ with 2-furylstannane gave the cross-coupling products in rather low yields. Diphenyltellurium dichloride **1a** reacted with 2-furyltributylstannane **2b** in the presence of $PdCl_2$ (10 mol%) and Cs_2CO_3 (2 equiv.) in MeCN at room temperature for 3 h to afford 2-phenylfuran (**3a**)[6] in 89% isolated yield. Under the same conditions but with CuI (10 mol%) as catalyst at 70 °C the reaction gave **3a** in 72% yield (method B in entry 1, Table 1). We tested various copper catalysts to discover a palladium-free Stille protocol, and the cross-coupling of the organostannane **2b** with **1a** was achieved at 70 °C. Of the catalysts used, CuI (10 mol%) was the most preferable among CuI, CuBr, and $Cu(OAc)_2$. As base, Cs_2CO_3 was more suitable than K_2CO_3, Na_2CO_3 and NaOMe. The solvent MeCN was the best choice, presumably because of the solubility of organotellurium compounds. The reaction of di(*p*-methoxyphenyl)tellurium dichloride **1b** with **2b** in the presence of $PdCl_2$ at room temperature and CuI at 70 °C proceeded to give 2-(*p*-methoxyphenyl)furan **3b**[7] in 89 and 68% yields, respectively (methods A and B in entry 2). This coupling method was also applied to alkenyl-substituted stannane **2d**. The reaction of **1b** with β-(*E*)-styrylstannane **2d** gave the substituted stilbene **3d**[8] (entry 4). When di[β-(*Z*)-styryl]tellurium dichloride **1c** was treated with 2-furylstannane **2b**, 2-β-(*Z*)-styryl substituted furan **3e** was readily obtained in 70 and 56% yields, respectively (methods A and B in entry 5). The (*Z*)-stereochemistry of **3e** was confirmed by the coupling constant $J = 12.1$ Hz for the vinylic protons.



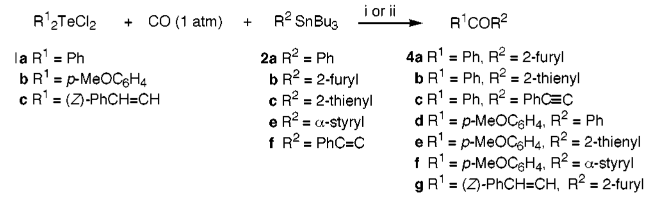
Scheme 1 *Reagents and conditions:* i (method A), $PdCl_2$ (10 mol%), MeCN, Cs_2CO_3 (2 equiv.), room temp., 3 h; ii (method B), CuI (10 mol%), MeCN, Cs_2CO_3 (2 equiv.), 70 °C, 7 h.

We then extended this reaction to carbonylative cross-coupling with organostannanes (Scheme 2). The diphenyltellurium dichloride **1a** was successfully coupled with 2-furyltributylstannane **2b** under atmospheric pressure of CO under palladium or copper catalysis to furnish 2-benzoylfuran **4a**[9] in 84 and 63% isolated yields (methods A and B in entry 7).

Table 1 Pd- and Cu-catalyzed cross-coupling and carbonylative cross-coupling of organotellurium dichloride with organostannanes

Entry	Organotellurium compounds	Organostannanes	Reaction conditions[a]	Products	Isolated yields (%)
Cross-coupling					
1	**1a**	**2b**	A	**3a**	89
			B		72
2	**1b**	**2b**	A	**3b**	89
			B		68
3	**1b**	**2c**	A	**3c**	88
			B		65
4	**1b**	**2d**	A	**3d**	81
5	**1c**	**2b**	A	**3e**	70
			B		56
6	**1c**	**2c**	A	**3f**	76
			B		61
Carbonylative cross-coupling					
7	**1a**	**2b**	A	**4a**	84
			B		63
8	**1a**	**2c**	A	**4b**	85
			B		65
9	**1a**	**2f**	A	**4c**	82
10	**1b**	**2a**	A	**4d**	83
11	**1b**	**2c**	A	**4e**	83
			B		70
12	**1b**	**2e**	A	**4f**	90
13	**1c**	**2b**	A	**4g**	70
			B		52

[a] A: $PdCl_2$ (10 mol%), Cs_2CO_3 (2 equiv.), room temp. B: CuI (10 mol%), Cs_2CO_3 (2 equiv.), 70 °C. Carbonylative cross-coupling carried out under atmospheric pressure of CO.



Scheme 2 *Reagents and conditions:* i (method A), $PdCl_2$ (10 mol%), MeCN, Cs_2CO_3 (2 equiv.), room temp., 3 h; ii (method B), CuI (10 mol%), MeCN, Cs_2CO_3 (2 equiv.), 70 °C, 7 h.

Treatment of **1a** with 2-thienyltributylstannane **2c** under the same conditions afforded 2-benzoylthiophene **4b**[10] in 85% yield (entry 8). This carbonylative coupling was also applied to alkynyltributylstannane **2f** to provide alkynyl-substituted ketone **4c** (entry 9).[11] For the di(*p*-methoxyphenyl)tellurium dichloride **1b**, phenyltributylstannane **2a** and 2-thienyltributylstannane **2c** were smoothly coupled to give ketones **4d**[11] and **4e**,[11] respectively, in 83% yield (entries 10 and 11). When the tellurium dichloride **1b** was treated with α-styryltributylstannane **2e**, unexpectedly the carbonylative cross-coupled product **4f**[12] was obtained as the sole product in 90% yield without any *cine*-substitution[13] product (entry 12). Finally, di[β-(*Z*)-styryl]tellurium dichloride **1c** was successfully coupled with **2b** under CO to afford β-(*Z*)-styryl-substituted ketone **4g**[14] in 70 and 52% yields, respectively (methods A and B in entry 13).

In considering a plausible mechanism for the cross-coupling it is presumed that oxidative addition of organotellurium compounds with Pd^0 or Cu^I gives $R^1PdTeR^2Cl_2$ or $R^1CuTeR^2Cl_2$, which is subjected to transmetallation with stannanes followed by reductive elimination to afford the cross-coupled products.

In summary, the palladium- and copper-catalyzed cross-coupling and carbonylative cross-coupling of diorganotellurium dichlorides with organostannanes were achieved under mild conditions in good to moderate yields.

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Notes and references

1 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508; T. N. Mitchell, *Synthesis*, 1992, 803; V. Farina, *Pure Appl. Chem.*, 1996, **68**, 73.

2 R. M. Moriarty and W. R. Epa, *Tetrahedron Lett.*, 1992, **33**, 4095; R. J. Hinkle, G. T. Poulter and P. T. Stang, *J. Am. Chem. Soc.*, 1993, **115**, 11 626; S.-K. Kang, H.-W. Lee, J.-S. Kim and S.-C. Choi, *Tetrahedron Lett.*, 1996, **37**, 3723; S. K. Kang, H.-W. Lee, S.-B. Jang, T.-H. Kim and J.-S. Kim, *Synth. Commun.*, 1996, **26**, 4311.

3 S.-K. Kang H.-C. Ryu and S.-C. Choi, *Chem. Commun.*, 1998, 1317.

4 (*a*) K. Ohe, H. Takahashi, S. Uemura and N. Sugita, *J. Org. Chem.*, 1987, **52**, 4859; (*b*) Y. Nishibayashi, C.-S. Cho, K. Ohe and S. Uemura, *J. Organomet. Chem.*, 1996, **526**, 335; (*c*) Y. Nishibayashi, C.-S. Cho, K. Ohe and S. Uemura, *J. Organomet. Chem.*, 1996, **507**, 197.

5 N. Petragnani, in *Tellurium in Organic Synthesis*, Academic Press, 1994 and references therein. General procedure as follows. Diphenyltellurium dichloride (**1a**): $TeCl_4$ (40 mmol) and PhHgCl (80 mmol) were heated under reflux in anhydrous dioxane (100 ml) for 2 h. The solution is cooled to 10 °C and the $HgCl_2$ dioxane precipitate filtered off and washed with cold dioxane (15 ml). The filtrate was poured with stirring into 1% ice-cold HCl (400 ml). The dichlorides precipitate as crystalline solids and were recrystallized from benzene–light petroleum (bp 30–60 °C. Di[β-(*Z*)-styryl]tellurium dichloride (**1c**): $NaBH_4$ (9 mmol) was added in small portions to a stirred suspension of Te (3 mmol) in EtOH (15 ml), and THF (5 ml) was added to the hot mixture, which was then refluxed. After 15 min the mixture turned dark violet and the reflux was continued until all the Te had disappeared. The heat source was removed and the phenylacetylene (7.8 mmol) added. When the color changed to yellow, the mixture was cooled at room temperature, diluted with EtOAc (50 ml) and washed first with saturated aqueous NH_4Cl (3 × 30 ml) and then with brine (3 × 30 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated in a rotary evaporator. The residue dissolved in a small amount of $CHCl_3$ was treated dropwise, while cooling (ice bath) and stirring, with a solution of an equimolar amount of SO_2Cl_2 in the same solvent. By addition of a large excess of light petroleum (bp 30–60 °C) the dihalide precipitates as a crystalline solid.

6 A. Pelter, M. Rowlands and G. Clements, *Synthesis*, 1987, 51.

7 S.-K. Kang, J.-S. Kim and S.-C. Choi, *J. Org. Chem.*, 1997, **62**, 4208.

8 S.-K. Kang, T.-G. Baik and S.-Y. Song, *Synlett*, 1999, **3**, 327.

9 G. Zadel and E. Breitmaier, *Angew. Chem., Int. Ed. Engl.*, 1992, **23**, 1070.

10 S.-K. Kang, K.-H. Lim, P.-S. Ho, S.-K. Yoon and H.-J. Son, *Synth. Commun.*, 1998, **28**, 1481.

11 S.-K. Kang, P.-S. Ho, S.-K. Yoon, J.-C. Lee and K.-J. Lee, *Synthesis*, 1998, 823.

12 *Selected data* for **4f**: δ_H(400 MHz, $CDCl_3$) 7.91 (dd, 2 H, *J* 4.0, 2.0), 6.91 (dd, 2 H, *J* 4.0, 2.0), 4.92 (d, 1 H, *J* 2.8), 4.67 (d, 1 H, *J* 2.8), 3.92 (q, 2 H, *J* 7.1), 3.86 (s, 3 H), 1.40 (t, 3 H, *J* 7.1); *m/z* 235 (M^+), 234 (M), 162 (34%), 135 (100), 107 (10), 92 (19), 77 (27) (HRMS: calc. for $C_{13}H_{14}O_4$: 234.0887, found: 234.0889).

13\. K. Kikukwa, H. Uemura and T. Matsuda, *J. Organomet. Chem.*, 1986, **311**, c44; G. Stork and R. C. A. Isaacs, *J. Am. Chem. Soc.*, 1990, **112**, 7399; C. A. Busacca, J. Swestock, R. E. Johnson, T. R. Bailey, L. Musza and C. A. Rodger, *J. Org. Chem.*, 1994, **59**, 7553; V. Farina and M. A. Hossian, *Tetrahedron Lett.*, 1996, **37**, 6997; S.-H. Chen, *Tetrahedron Lett.*, 1997, **38**, 4741.

14 *Selected data* for **4a**: δ_H(500 MHz, $CDCl_3$) 6.49 (m, 1 H), 6.85 (d, 1 H, *J* 12.1), 6.99 (d, 1 H, *J* 12.1), 7.29 (m, 1 H), 7.32 (m, 3 H), 7.50 (m, 3 H); ν_{max}(KBr)/cm^{-1} 3132, 2340, 1660, 1620, 1572, 1465; *m/z* 198 (M^+), 197 (M, 100%), 141 (31), 103 (25).

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