

Palladium-catalyzed cross-coupling of organolead compounds with organostannanes

Suk-Ku Kang,*† Hyung-Chul Ryu and Sang-Chul Choi

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 400-746, Korea

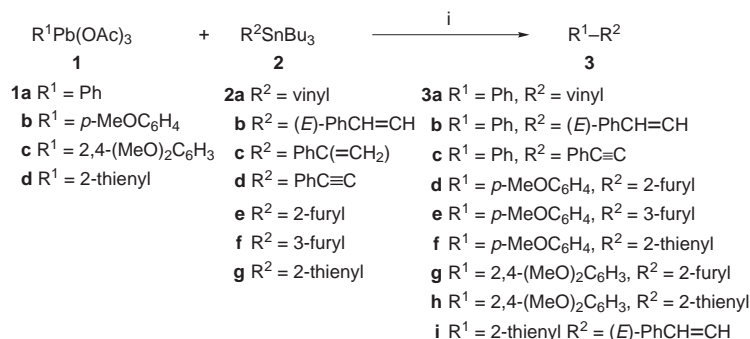
The palladium-catalyzed cross-coupling of organolead triacetates with organostannanes has been accomplished in the presence of Pd₂(dba)₃·CHCl₃ (5 mol%) and NaOMe (5 equiv.) in MeOH–MeCN (1 : 1) under mild conditions.

The palladium-catalyzed cross-coupling of organostannanes with aryl or vinyl halides and triflates, known as the Stille reaction,¹ has become a versatile tool in organic synthesis. Main group metals such as lead(IV),² bismuth³ and thallium⁴ have been of limited use in cross-coupling reactions. Recently, Pinhey² reported the arylation, alkenylation and alkynylation of organolead(IV) tricarboxylates with soft carbon nucleophiles. As an alternative to organic electrophiles, hypervalent iodonium compounds were employed in the cross-coupling with organostannanes.⁵ However, the coupling reaction of organolead compounds as electrophiles with organostannanes is not known. Here we report the cross-coupling of organostannanes with organolead(IV) compounds.

Initially, we examined the cross-coupling of phenyllead triacetate **1a**⁶ with vinyl tributylstannane **2a** to determine the optimum reaction conditions. After series of fruitless experiments, we found that the use of NaOMe as a base was crucial in this coupling. Of the catalysts Pd₂(dba)₃·CHCl₃, Pd(OAc)₂ and PdCl₂ tested, Pd₂(dba)₃·CHCl₃ was the best. Even though CHCl₃ was also effective, the solvent system MeOH–MeCN

(1 : 1) was most suitable. To avoid homocoupling, CuI (10 mol%) was added as a cocatalyst (Scheme 1).⁷

Phenyllead triacetate **1a** was reacted with vinyl tributylstannane **2a** in the presence of NaOMe (5 equiv.) using Pd₂(dba)₃·CHCl₃ (5 mol%) and CuI (10 mol%) as catalysts in MeOH–MeCN (1 : 1) at room temperature for 2 h to afford styrene **3a** as the sole product in 80% yield (entry 1, Table 1). Under the same conditions the reaction of **1a** with the β-styrylstannane **2b** gave the coupled product (*E*)-β-stilbene **3b** in 72% yield (entry 2). When phenyllead triacetate **1a** was treated with α-styrylstannane **2c**, (*E*)-β-stilbene **3b** was also obtained as the sole product via the mechanism of *cis* substitution⁸ in 40% yield (entry 3). For the alkynylstannane **2d**, the reaction with **1a** gave the coupled product **3c** in 79% yield (entry 4). When the same reaction was conducted in CHCl₃ as the only solvent, the coupled product **3c** was obtained in 45% yield along with the homocoupled product (30%).⁹ Treatment of 2-furyl(tributyl)stannane **2e**, 3-furyl(tributyl)stannane **2f**, and 3-thienyl-substituted stannane **2g** with *p*-methoxyphenyllead triacetate **1b**¹⁰ afforded the substituted furans **3d**,¹¹ **3e**¹² and thiophene **3f**¹³ in 73, 70 and 85% yields, respectively (entries 5–7).[‡] For the coupling of **1b** with 2-furyl stannane **2e** under the same conditions without addition of CuI as catalyst, the coupled product **3e** was obtained in 60% yield after 7 h along with the homocoupled product (25%). However, the addition of CuI (10



Scheme 1 Reagents and conditions: i, Pd(dba)₃·CHCl₃ (5 mol%), CuI (10 mol%), NaOMe (5 equiv.), MeOH–MeCN (1 : 1)

Table 1 Palladium-catalyzed cross-coupling of organostannanes with organolead triacetates

Entry	Organolead compounds	Organostannanes	T/°C	t/h	Product	Isolated yield (%) ^a
1	1a	2a	room temp.	2	3a	80 (trace)
2	1a	2b	room temp.	2	3b	72 (trace)
3	1a	2c	60	3	3b	40
4	1a	2d	room temp.	2	3c	79 (10)
5	1b	2e	room temp.	2	3d	73 (10)
6	1b	2f	60	2	3e	70 (trace)
7	1b	2g	60	2	3f	85 (10)
8	1c	2e	room temp.	3	3g	72 (trace)
9	1c	2g	room temp.	3	3h	73 (trace)
10	1d	2b	60	2	3i	62 (10)

^a The yields in parentheses are the yields of the homocoupling products, which are easily separated by column chromatography.

mol%) improved the yield to 73% yield with reduced reaction time (2 h) and reduced homocoupling (10%). The 2,4-dimethoxyphenyllead triacetate **1c**¹⁴ was also coupled with 2-furyl and 2-thienyl substituted stannanes **2e** and **2g** at room temperature for 3 h to afford the coupled products **3g**§ and **3h**¹⁵ in 72 and 73% yields, respectively (entries 8 and 9). Finally, 2-thienyllead triacetate **1d**¹⁶ was reacted with (*E*)- β -styrylstannane **2b** to give the coupled product **3i**¹⁷ in 62% yield (entry 10). The results are summarized in Scheme 1 and Table 1.

Although the detailed mechanism for the role of NaOMe remains to be elucidated, it is presumed that organolead trimethoxide $\text{RPb}(\text{OMe})_3$ is formed¹⁸ and drives facile oxidative addition¹⁹ with Pd^0 to give polar reactive intermediate $\text{RPdPb}(\text{OMe})_3$, which allows the transmetalation and coupling to proceed under mild conditions.

A typical procedure is as follows: To a stirred solution of *p*-methoxyphenyllead triacetate **1b** (140 mg, 0.28 mmol) and NaOMe (77 mg, 1.42 mmol) in MeOH–MeCN (1 : 1, 3 ml) was added $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$ (14 mg, 5 mol%) and CuI (5 mg, 10 mol%), followed by 2-thienyl(tributyl)stannane **2g** (100 mg, 0.27 mmol) *via* syringe at room temperature under N_2 , and the reaction mixture was stirred at 60 °C for 2 h and cooled to room temperature. The reaction mixture was extracted with Et_2O (20 ml), washed three times with water, dried over anhydrous MgSO_4 and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, $R_f = 0.28$) to afford the coupled product **3f** (44 mg, 85%).

In conclusion, the palladium-catalyzed cross-coupling reaction of organolead triacetates with organostannanes was achieved under mild conditions.

The authors wish to acknowledge the financial support of the Korea Research Foundation in the Program Year 1997.

Notes and References

† E-mail: skkang@chem.skku.ac.kr

‡ Selected data for **3e**: TLC, SiO_2 , hexanes, $R_f = 0.36$; δ_{H} (400 MHz, CDCl_3) 3.83 (s, 3 H), 6.65 (m, 1 H), 6.92 (m, 2 H), 7.42 (m, 3 H), 7.65 (s, 1 H); ν_{max} (neat)/ cm^{-1} 3054, 2928, 1605, 1275; *m/e* (EI) 174 (100%), 159 (75), 131 (45), 77 (40).

§ Selected data for **3g**: TLC, SiO_2 , EtOAc–hexanes (1 : 10), $R_f = 0.37$; δ_{H} (400 MHz, CDCl_3) 3.96 (s, 3 H), 4.04 (s, 3 H), 6.59 (m, 1 H), 6.68 (m, 1 H), 6.70 (m, 1 H), 6.91 (m, 1 H), 7.54 (dd, 1 H), 7.87 (d, 1 H); ν_{max} (neat)/ cm^{-1} 3055, 2856, 1422, 1265, 896, 740; *m/z* (EI) 203 (100%), 188 (24), 161 (41), 102 (119).

1 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508–524; T. N. Mitchell, *Synthesis*, 1992, 803; V. Farina, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G.

- Wilkinson, Pergamon, New York, 1995, vol. 12, ch. 3, 4; V. Farina, *Pure Appl. Chem.*, 1996, **68**, 73.
- 2 J. T. Pinhey, *Aust. J. Chem.*, 1991, **44**, 1353; J. T. Pinhey, *Pure Appl. Chem.*, 1996, **68**, 819; S. Hashimoto, Y. Miyazaki, T. Shinoda and S. Ikegami, *J. Chem. Soc., Chem. Commun.*, 1990, 1100.
- 3 Y. Matano and H. Suzuki, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2673.
- 4 R. C. Larock and C. A. Fellows, *J. Am. Chem. Soc.*, 1982, **104**, 1900; R. C. Larock, S. Varaprah, H. H. Lau and C. A. Fellows, *J. Am. Chem. Soc.*, 1984, **106**, 5274; E. C. Tayler and A. Mckillop, *Acc. Chem. Res.*, 1970, **3**, 338; R. C. Larock and H. Yang, *Synlett*, 1994, 748.
- 5 R. M. Moriarty and W. R. Epa, *Tetrahedron Lett.*, 1992, **33**, 4095; R. J. Hinkle, G. T. Poulter and P. J. 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.
- 6 J. Morgan and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1990, 715.
- 7 The CuCl-catalyzed homocoupling of vinyl- and aryl-lead diacetates was reported by Pinhey see J. Morgan, C. J. Parkinson and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1994, 3361.
- 8 K. Kikukawa, H. Umekawa 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. Hossain, *Tetrahedron Lett.*, 1996, **37**, 6997.
- 9 The substituted lead(IV) triacetates undergo homocoupling in the presence of $\text{Pd}_2(\text{dba})_3\text{-CHCl}_3$ (5 mol%) in CHCl_3 at room temperature for 10 min. See, S-K. Kang, U. Shivkumar, C. Ahn, S-C. Choi and J-S. Kim, *Synth. Commun.*, 1997, **27**, 1893.
- 10 *p*-Methoxyphenyllead triacetate **1b** was easily prepared from anisole by treatment with lead tetraacetate. See R. P. Kozyrod and J. T. Pinhey, *Org. Synth.*, 1984, **62**, 24.
- 11 S. Pelter, M. Rowlands and G. Clements, *Synthesis*, 1987, 51.
- 12 R. H. Young, R. L. Martin, N. Chinh, C. Mallon and R. H. Kayser, *Can. J. Chem.*, 1972, **50**, 932.
- 13 L. J. Baldwin, S. Pakray, R. N. Castle and M. L. Lee, *J. Heterocyclic Chem.*, 1985, **22**, 1667.
- 14 L. C. Willemsens, D. de V. J. Spierenburg and J. Wolters, *J. Organomet. Chem.*, 1972, **39**, C61.
- 15 T. Sone, R. Yokoyama, Y. Okuyama and K. Sato, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 83.
- 16 H. C. Bell, J. R. Kalman, J. T. Pinhey and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1521.
- 17 A. Kasahara, T. Izumi and T. Ogihara, *J. Heterocyclic Chem.*, 1989, **26**, 597.
- 18 Recently, it was reported that the modification of ligands influences the efficiency of the metal–metal exchange: C. J. Parkinson, J. T. Pinhey and M. J. Stoermer, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1911.
- 19 The oxidative addition of organostannanes to a palladium(0) complex is known: E. Shirakawa, H. Yoshida and T. Hiyama, *Tetrahedron Lett.*, 1997, **38**, 5177.

Received in Cambridge, UK, 14th April 1998; 8/027261