

Palladium-Catalyzed Coupling of Organolead Compounds with Olefins

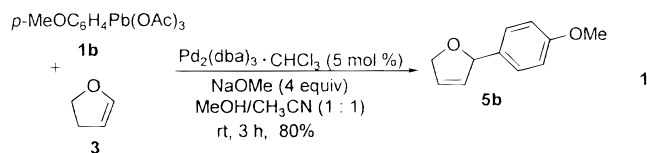
Suk-Ku Kang,* Sang-Chul Choi, Hyung-Chul Ryu, and Tokutaro Yamaguchi

Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus, Suwon 440-746, Korea

Received March 30, 1998

The palladium-catalyzed coupling of organic electrophiles (i.e., halides and triflates) with alkenes (Heck-type coupling)¹ is now recognized to be an extremely useful and convenient method for the formation of carbon–carbon bonds in the synthesis of valuable products under mild conditions. The introduction of new reagents would expand the scope of the cross-coupling and the Heck-type reactions. Main group metals such as lead(IV),² bismuth,³ and thallium⁴ have been of limited use as coupling reagents. Recently, Pinhey² reported the arylation, alkenylation, and alkynylation of organolead(IV) tricarboxylates with soft carbon nucleophiles. As an alternative to the use of organic electrophiles, hypervalent iodonium compounds were employed in the coupling with olefins.⁵ However, to the best of our knowledge, coupling reactions of organolead compounds as electrophiles with olefins have not been known. Here, we wish to report the coupling of olefins with organolead(IV) compounds.

To determine optimum reaction conditions for the coupling of olefins with organolead triacetates, a series of experiments were performed on the coupling of 2,3-dihydrofuran(**3**) with (*p*-methoxyphenyl)lead triacetate (**1b**). After a series of fruitless experiments, we found that the use of NaOMe (4 equiv) as a base was critical in this type of coupling. By the use of bases tested, KOAc, Et₃N, and K₂CO₃, the homocoupled product 4,4'-dimethoxybiphenyl was formed as major product.⁶ Among the palladium catalysts Pd(OAc)₂, PdCl₂(CH₃CN)₂, Pd(PPh₃)₄, Pd(OAc)₂, PdCl₂(dppf), and Pd₂(dba)₃·CHCl₃, Pd₂(dba)₃·CHCl₃ was the best choice. As a suitable solvent, the cosolvent CH₃CN/MeOH (1:1) was the most preferable, even though CH₃CN/PhH (1:1) was also effective (eq 1).



Accordingly, the phenyllead triacetate (**1a**)⁷ was reacted with styrene (**2a**) at room temperature in the presence of Pd₂(dba)₃·CHCl₃ (5 mol %) and NaOMe(4 equiv) to afford

Table 1. Heck-Type Reactions of Organolead Triacetates with Olefins

Entry	Organolead Compounds	Olefins	Temp(°C)	Time(h)	Product	Yield(%) ^{a,b}
1	PhPb(OAc) ₃ 1a		rt	3		75
2	1a		60	4		71
3	1a		80	12		54(20)
4	1a		rt	2		68(10)
5	1b		80	10		70
6	1b		80	10		75
7	<i>p</i> -MeOC ₆ H ₄ Pb(OAc) ₃ 1b		rt	3		80
8	2-ThienylPb(OAc) ₃ 1c		rt	2		65(10)
9			rt	6		74

^a The isolated yields. ^b The numbers in parentheses represent the yields of the homocoupling.

the coupled product *trans*-stilbene (**4a**) in 75% yield (entry 1, Table 1). Under the same conditions, treatment of **1a** with methyl acrylate (**2b**) at 60 °C for 4 h gave (*E*)-methyl cinnamate (**4b**) in 71% yield (entry 2). Phenyllead triacetate (**1a**) underwent facile coupling with diol olefin **2c** without any formation of ketone resulting from β-PdH elimination⁸ to give **4c** (entry 3). The palladium-catalyzed phenylation of 2,3-dihydrofuran (**3**) was accomplished with **1a** to give the thermodynamically less stable 2-substituted 2,5-dihydrofurans **5a** as a major product (entry 4).⁹ When the substituted phenyllead acetate **1b**¹⁰ was reacted with the acetonide **2d** under similar conditions, the coupled product **4d**¹¹ was readily obtained in 70% yield (entry 5). The diol cyclic carbonate **2e**¹² was also smoothly coupled with (*p*-methoxyphenyl)lead triacetate to afford the substituted cyclic carbonate **4e**¹¹ without ring opening (entry 6).¹³ For the 2,3-dihydrofuran, the palladium-catalyzed arylation gave the kinetically favored product **5b** in 80% yield (entry 7). This coupling was applied to (2-thienyl)lead triacetate(**1c**),¹⁴

(8) In the case of allylic alcohols, palladium-catalyzed reaction of organic halides usually affords β-substituted ketones or aldehydes rather than the β-substituted allylic alcohols. See: (a) Melpolder, J. B.; Heck, R. F. *J. Org. Chem.* **1976**, *41*, 265–272. (b) Tamara, Y.; Yamada, Y.; Yoshida, Z.-I. *Tetrahedron* **1979**, *35*, 329–340 and references therein.

(1) (a) Heck, K. F. *Acc. Chem. Res.* **1979**, *12*, 146–151. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411.

(2) (a) Pinhey, J. T. *Aust. J. Chem.* **1991**, *44*, 1353–1382. (b) Pinhey, J. T. *Pure Appl. Chem.* **1996**, *68*, 819–824. (c) Hashimoto, S.; Miyazaki, Y.; Shinoda, T.; Ikegami, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1100–1102.

(3) Matano, Y.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2673–2681.

(4) (a) Larock, R. C.; Fellows, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 1900–1907. (b) Larock, R. C.; Varaprah, S.; Lau, H. H.; Fellows, C. A. *Ibid.* **1984**, *106*, 5274–5284. (c) Tayler, E. C.; Mckillop, A. *Acc. Chem. Res.* **1970**, *3*, 338–346. (d) Larock, R. C.; Yang, H. *Synlett* **1994**, 748–750.

(5) (a) Moriarty, R. M.; Epa, W. R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1991**, *113*, 6315–6317. (b) Kang, S.-K.; Lee, H.-W.; Jang, S.-B.; Kim, T.-H.; Pyun, S.-J. *J. Org. Chem.* **1996**, *61*, 2604–2605.

(6) The substituted lead(IV) triacetates undergo homocoupling in the presence of Pd₂(dba)₃·CHCl₃ (5 mol %) in CHCl₃ at room temperature for 10 min. See: Kang, S.-K.; Shivkumar, U.; Ahn, C.; Choi, S.-C.; Kim, J.-S. *Synth. Commun.* **1997**, *27*, 1893–1897.

(7) Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 715–720.

which was reacted with **3** to give **5c** (entry 8). Finally, the reaction of (2,4-dimethoxyphenyl)lead triacetate (**1d**)¹⁵ with styrene (**2a**) proceeded smoothly to give the coupled product **4f**¹¹ in 74% yield (entry 9).

The typical procedure is as follows. To a stirred solution of (*p*-methoxyphenyl)lead triacetate (**1b**) (200 mg, 0.40 mmol) and NaOMe (88 mg, 1.60 mmol) in CH₃CN/MeOH (1:1, 6 mL) was added Pd₂(dba)₃·CHCl₃ (20 mg, 5 mol %) followed by 2,3-dihydrofuran (**3**) (34 mg, 0.48 mmol) via syringe, and the reaction mixture was stirred at room

(9) Recently, palladium-catalyzed arylation and alkenylation of 2,3-dihydrofuran has attracted considerable interest since it offers the possibility of carrying out asymmetric coupling reactions. Depending on the reaction conditions, the thermodynamically more stable 2-substituted 2,3-dihydrofurans or the less stable 2-substituted 2,5-dihydrofurans can be formed. 2,5-Dihydrofuran formation: (a) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1990**, *55*, 407–408. (b) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047–2050. (c) Larock, R. C.; Gong, W. H.; Baker, B. E. *Tetrahedron Lett.* **1989**, *30*, 2603–2606. (d) Kang, S.-K.; Yamaguchi, T.; Kim, J.-S.; Choi, S.-C.; Ahn, C. *Synth. Commun.* **1997**, *27*, 1105–1110. Asymmetric version: (e) Louseleur, O.; Meire, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 200–203. (f) Kurihara, Y.; Sedeoka, M.; Shibasaki, M. *Chem. Pharm. Bull.* **1994**, *42*, 2357–2359. (g) Hillers, S.; Reiser, O. *Synlett.* **1997**, *27*, 1105–1110. 2,3-Dihydrofuran formation: (h) Zhang, H.-C.; Daves, G. D., Jr. *Organometallics* **1993**, *12*, 1499–1500. (i) Hillers, S.; Sartori, S.; Reiser, O. *J. Am. Chem. Soc.* **1996**, *118*, 2087–2088. Asymmetric version: (j) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1419–1421. (k) Ozawa, F.; Hayashi, T. *J. Organomet. Chem.* **1992**, *428*, 267–277. (l) Ozawa, F.; Kobatake, Y.; Hayashi, T. *Tetrahedron Lett.* **1993**, *34*, 2505–2508. (m) Ozawa, F.; Kubo, A.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 1485–1488. (n) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K.-i. *Organometallics* **1993**, *12*, 4188–4196.

(10) (*p*-Methoxyphenyl)lead triacetate **1b** was easily prepared from anisole by treatment of lead(IV) tetraacetate. See: Kozyrod, R. P.; Pinhey, J. T. *Org. Synth.* **1984**, *62*, 24–29.

(11) Satisfactory spectral data were obtained in accord with the structure. The HRMS data are as follows for the new compounds. **4d**: HRMS calcd for C₂₂H₂₆O₄ 354.1763, found 354.1831. **4e**: HRMS calcd for C₂₀H₂₀O₃ 340.1283, found 340.1311. **4f**: HRMS calcd for C₁₆H₁₆O₂ 240.1150, found 240.1150.

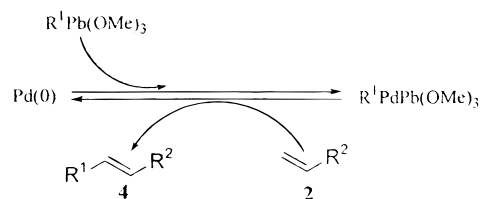
(12) Kang, S.-K.; Lee, D.-H.; Sim, H.-S.; Lim, J.-S. *Tetrahedron Lett.* **1993**, *34*, 91–94.

(13) Palladium-catalyzed phenylation of allylic cyclic carbonates with diphenyliodonium tetrafluoroborate without no occurrence of ring opening was recently reported: Kang, S.-K.; Jung, K.-Y.; Park, C.-H.; Jang, S.-B. *Tetrahedron Lett.* **1995**, *36*, 8047–8050.

(14) Willemsens, L. C.; Spierenburg, D. de V. J.; Wolters, J. *J. Organomet. Chem.* **1972**, *39*, C61–C62.

(15) Bell, H. C.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Aust. J. Chem.* **1979**, *32*, 1521–1530.

Scheme 1. Mechanistic Rationale



temperature for 3 h. The reaction mixture was extracted with ether (20 mL) and washed with water three times (20 mL × 3), and the organic layer was dried over anhydrous MgSO₄ evaporated in vacuo. The crude product was separated by SiO₂ column chromatography (EtOAc/hexanes 1:10, R_f = 0.32) to afford the coupled product **5b** (57 mg, 80%).

Although the detailed mechanism for the role of NaOMe remains to be elucidated, it is presumed that organolead trimethoxide RPb(OMe)₃ is formed^{16,17} and drives facile oxidative addition with Pd(0) to give polar and reactive intermediate RPdPb(OMe)₃,¹⁸ which allow the coupling under mild conditions, as illustrated in Scheme 1.

In conclusion, the palladium-catalyzed coupling reactions of organolead triacetates with olefins were achieved under mild conditions. The methods described herein are useful in terms of reaction conditions and efficiency.

Acknowledgment. The generous financial support from Korea Science and Engineering Foundation through the Organic Chemistry Research Center (KOSEF-OCRC) and Ministry of Education (BSRI-97-3420) is gratefully acknowledged.

Supporting Information Available: Experimental procedures and analytical data for the compounds (2 pages).

JO980577N

(16) It was reported that the modification of ligands influences the efficiency in metal–metal exchange: Parkinson, C. J.; Pinhey, J. T.; Stoermer, M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1911–1915.

(17) Presumably, the formation of RPb(OMe)(OAc)₂ or R₂Pb(OMe)₂(OAc)₂ cannot be ruled out.

(18) The oxidative addition of organostannanes to a palladium(0) complex has been known: Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177–5180.