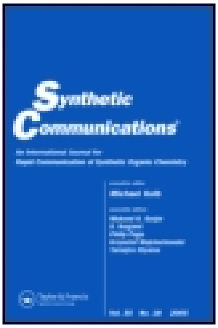

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Palladium-Catalyzed Cross-Coupling of Organolead Compounds with Hypervalent Iodonium Salts

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PALLADIUM-CATALYZED CROSS-COUPLING OF ORGANOLEAD COMPOUNDS WITH HYPERVALENT IODONIUM SALTS

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Abstract: The palladium-catalyzed cross-coupling of hypervalent iodonium salts with organolead triacetates was achieved with $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol %) in the presence of NaOMe (2 equiv) in $CHCl_3$ at room temperature.

The palladium-catalyzed cross-coupling of organic electrophiles (i.e. halides and triflates) with organostannanes (Stille coupling),[1] organoboranes (Suzuki coupling),[2] and organozinc compounds[3] is now recognized to be an extremely powerful tool in carbon-carbon bond formations. As an alternative to organic electrophiles, we have reported[4,5] the palladium-catalyzed cross-coupling of hypervalent iodonium salts[6] with organostannanes and organoboranes. Main group metals such as lead(IV),[7] bismuth,[8] and thallium[9] have been of limited use as coupling reagents. The arylation, alkenylation, and alkynylation of organolead(IV) tricarboxylates with soft carbon nucleophiles such as active methylene compouds were reported.[7] Recently we have reported the cross-

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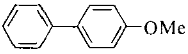
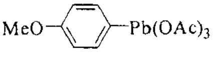
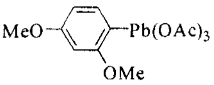
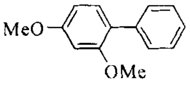
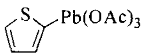
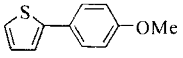
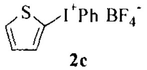
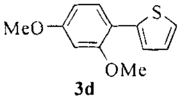
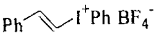
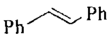
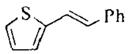
coupling of organolead tiracetes with organostannanes and boranes.[10] However, the cross-coupling reactions of organolead compounds with hypervalent iodonium salts have not been known. Here we wish to report the cross-coupling of organolead compounds with hypervalent iodonium tetrafluoroborates (eq. 1).

$$\mathrm{Ar^1I^+Ph\ BF_4^-} + \mathrm{Ar^2Pb(OAc)_3} \xrightarrow[\substack{\mathrm{NaOMe\ (2\ equiv)} \\ \mathrm{CHCl_3,\ rt} \\ \mathrm{3\ h}}]{\mathrm{Pd_2(dba)_3\cdot CHCl_3\ (5\ mol\ \%)}} \mathrm{Ar^1 - Ar^2} \qquad (1)$$

To determine the optimum reaction conditions we have examined the cross-coupling of *p*-methoxyphenyllead triacetate (**1b**)[11] with diphenyliodonium tetrafluoroborate (**2a**). After a series of experiments, we found that the addition of NaOMe is critical. As the solvent, $CHCl_3$ was the best choice. Of the catalysts tested $Pd_2(dba)_3\cdot CHCl_3$, $Pd(OAc)_2$, and $PdCl_2$, $Pd_2(dba)_3\cdot CHCl_3$ was most suitable. Phenyllead triacetate (**1a**)[12] reacted with *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**2b**) in the presence of NaOMe (2 equiv) and $Pd_2(dba)_3\cdot CHCl_3$ (5 mol %) in $CHCl_3$ at room temperature for 3 h to afford the *p*-methoxybiphenyl (**3a**) in 73% yield along with 10% of biphenyl (entry 1 in Table 1).[13] Under the same conditions, treatment of *p*-methoxyphenyllead triacetate (**1b**) with diphenyl iodonium tetraflouroborate (**2a**) gave the cross-coupled product **3a** in 63% yield and 4,4'-dimethoxybiphenyl, the homocoupled product of **1b**, which was easily separable from **3a** in 20% yield (entry 2). However, when 2,4-methoxyphenyllead tiracetate (**1c**)[14] was reacted with **2a**, the coupled product **3b** was obtained as the sole product in 70% yield (entry 3). For the coupling reaction of 2-thienyllead tiracetate (**1d**)[15] with **2b**, 2-(4-methoxyphenyl)thiophene (**3c**) was afforded in 72% yield together with *bis*thiophene as a minor product (entry 4). On the other hand, in the reaction of **1b** with 2-thienyl(phenyl)iodonium tetrafluoroborate (**2c**), the 2-thienyl group was coupled to provide the product **3c** in 65% yield with 4,4'-dimethoxybiphenyl as a minor product (entry 5). Treatment of **1c** with 2-thienyl-substituted iodonium salt **2c** gave the coupled product **3d** in 63% yield (entry 6). This coupling was also applied to alkenyliodonium salt **2d**. Coupling of **2d** with

Table 1. Palladium-Catalyzed Coupling of Organolead Triacetates with Hypervalent Iodonium Tetrafluoroborates

Entry	Organolead compounds	Iodonium Salts	Product	Yield(%)[a, b]
1	$PhPb(OAc)_3$ **1a**	p-$MeOC_6H_4I^+Ph\ BF_4^-$ **2b**	 **3a**	75 (10)
2	 **1b**	$Ph_2I^+\ BF_4^-$ **2a**	**3a**	62 (20)
3	 **1c**	**2a**	 **3b**	70 (trace)
4	 **1d**	**2b**	 **3c**	72 (10)
5	**1b**	 **2c**	**3c**	62 (25)
6	**1c**	**2c**	 **3d**	63 (23)
7	**1a**	 **2d**	 **3e**	70 (13)
8	**1d**	**2d**	 **3f**	72 (10)

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[a] The numbers in parentheses represent the yields of homocoupling of organolead compounds. [b] The yields refer to the isolated yields.

phenyllead triacetate (**1a**) and 2-thienyllead triacetate (**1d**) afforded **3e** and **3f** in 70 and 72% yields, respectively (entries 7 and 8). The results of the palladium-catalyzed cross-coupling of organolead compounds with hypervalent iodonium tetrafluoroborates are summarized in Table 1.

Although the detailed mechanism for the role of NaOMe remains obsecure, it is presumed that organolead intermediate $RPb(OMe)_2OAc$ is formed[16] and drives facile oxidative addition[17] with Pd(0) to give polar and reactive intemediate $RPdPb(OMe)_2OAc$, which allows the transmetallation with hypervalent iodonium compounds followed by reductive elimination to give the coupled product under mild conditions.

In conclusion, the palladium-catalyzed cross-coupling reaction of organolead tiracetate with hypervalent iodonium tetrafluoroborates was achieved under mild conditions.

Experimental Section

Typical procedures: Preparation of *p*-methoxybiphenyl (**3a**)

To a stirred solution of phenyllead triacetate (**1a**) (340 mg, 0.74 mmol) and NaOMe (66 mg, 1.23 mmol) in $CHCl_3$ (3 mL) was added $Pd_2(dba)_3{\cdot}CHCl_3$ (14 mg, 5 mol %) followed by hypervalent iodonium tetrafluoroborate (**2b**) (245 mg, 0.61 mmol) at room temperature under N_2 and the mixture was stirred at rt for 3 h. The reaction mixture was extracted with ether (20 mL) and washed 3 times with water, and the organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (hexanes, R_f = 0.17) to afford the coupled product **3a** (85 mg, 75%). TLC, SiO_2, hexanes, R_f = 0.17. m. p. 87.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.01 (m, 2H), 7.34 (m, 1H), 7.45 (m, 2H), 7.58 (m, 4H). IR (KBr) 3055, 1265, 1115 cm^{-1}. MS (EI): m/e (relative intensity) = 185 (13), 184 (M^+, 100), 169 (43), 141 (44), 115 (34).

(2,4'-Dimethoxy)biphenyl (**3b**): TLC, SiO_2, EtOAc/hexanes 1 : 30, R_f = 0.26. ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.87 (s, 3H), 6.58 (m, 2H), 7.27 (m, 2H), 7.39 (m, 2H), 7.51 (m, 2H). IR (KBr) 2835, 1415, 1260, 745 cm^{-1}. MS (EI): m/e (relative intensity) = 214 (M^+, 100), 199 (13), 129 (25).

2-(4-Methoxyphenyl)thiophene (**3c**):[18] TLC, SiO_2, hexanes, R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.94 (m, 2H), 7.08 (m, 1H), 7.23 (m, 2H), 7.57 (m, 2H). IR (KBr) 3102, 1603, 1433, 1218, 1019 cm^{-1}. MS (EI): m/e (relative intensity) = 191 (12), 190 (M^+, 100), 175 (80), 147 (29).

2-(2',4'-Dimethoxyphenyl)thiophene (**3d**):[19] TLC, SiO_2, EtOAc/hexanes 1 : 30, R_f = 0.25. ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.90 (s, 3H), 6.54 (m, 2H), 7.06 (m, 1H), 7.26 (m, 1H), 7.38 (m, 1H), 7.55 (dd, 1H, J = 6.6, 2.6 Hz). IR (KBr) 3052, 1710, 1408, 1266, 740 cm^{-1}. MS (EI): m/e (relative intensity) = 220(M^+, *100), 204 (34), 177 (29), 162 (20), 134 (28), 110 (12).*

trans-Stilbene (**3e**): TLC, SiO_2, heaxanes, R_f = 0.45. m. p. 121.5 - 123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 7.21 (m, 2H), 7.34 (m, 4H), 7.48 (m, 4H). IR (KBr) 3019, 1597, 1496, 1072, 962, 909, 765, 693 cm^{-1}. MS (EI): m/e (relative intensity) = 180 (M^+, 88), 179 (100), 178 (72), 165 (45), 89 (32), 76 (24).

2-(2-Phenylethenyl)thiphene (**3f**):[20] TLC, SiO_2, heaxanes, R_f = 0.40. ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, 1H, J = 16.1 Hz), 7.02 (dd, 1H, J = 5.1, 3.6 hz), 7.09 (d, 1H, J = 3.4 Hz), 7.24 (m, 3H), 7.35 (m, 2H). IR (KBr) 3055, 1597, 1447, 856 cm^{-1}. MS (EI): m/e (relative intensity) = 186 (M^+, 100), 185 (78), 184 (39), 170(15), 152 (23).

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