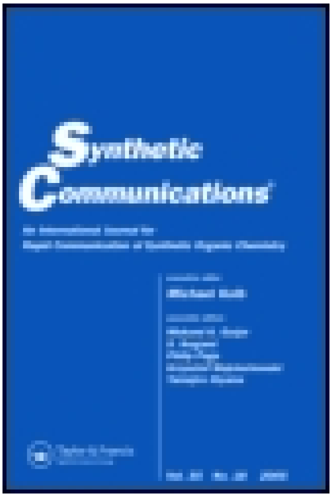

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Palladium- and Copper-Catalyzed Homocoupling of Organolead Compounds: Synthesis of Biaryls and Diynes

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PALLADIUM- AND COPPER-CATALYZED HOMOCOUPLING OF ORGANOLEAD COMPOUNDS: SYNTHESIS OF BIARYLS AND DIYNES

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Abstract: The palladium- and copper-catalyzed dimerization of aryl- and alkynyllead triacetates to form biaryls and dialkynes under mild conditions is described.

Functionalized symmetrical biaryls show specific properties as materials able to form semiconducting complexes[1] and as precursors of rigid liquid crystals.[2] The synthesis of biaryls from aryl halides can be achieved by transition metal catalysis in the presence of a reductant.[3] Thus, the synthesis of biaryls from aryl halides is catalyzed by nickel(II) complexes, in the presence of a chemical reductant such as zinc powder[3b-f] or upon electrochemical reduction catalyzed by palladium complexes.[4] Here we wish to report that aryl- and alkynyllead triacetates[5] are converted to biaryls and dialkynes[6,7] by treatment with a catalytic amount of palladium or copper catalyst (Eq. 1).

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$$\mathrm{RPb(OAc)_3} \xrightarrow{\text{Pd or Cu catalyst}} \text{R-R} \tag{1}$$

1a R = Ph
1b R = p-$CH_3C_6H_4$
1c R = p-$CH_3OC_6H_4$
1d R = 2-thienyl
2 R = PhC≡C

3a R = Ph
3b R = p-$CH_3C_6H_4$
3c R = p-$CH_3OC_6H_4$
3d R = 2-thienyl
4 R = PhC≡C

The results of palladium-catalyzed homocoupling of organolead compounds are summarized in Table 1. When phenyllead triacetate **1a** was reacted with a catalytic amount of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) in $CHCl_3$ at room temperature for 10 min, biphenyl (**3**) was produced in 68% yield (entry 1 in Table 1). Instead of palladium as a catalyst, copper was used as a catalyst in this homocoupling. Thus phenyllead triacetate (**1a**) was stirred with CuI (10 mol %) in dry DMF at 50 °C for 10 min to give biphenyl (**3a**) which was obtained in 68% yield (entry 2 in Table 1). By palladium and copper as catalysts, *p*-methylphenyllead triacetate **1b** was dimerized to afford **3b** in 65 and 62% yields, respectively (entries 3 and 4). By the same methods, *p*-methoxyphenyllead triacetate **1c** was coupled to afford **3e** (entries 5 and 6). Alternatively, 2-thienyllead triacetate (**1d**) was treated with palladium and copper as catalysts to afford the coupled product **3d** in 81 and 78% yields, respectively (entries 7 and 8). This method was also extended to alkynyl-substituted lead triacetate. The alkynyl-substituted lead triacetate **2** was reacted in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) and CuI (10 mol %) to give diacetylene **4** in 70 and 53% yields, respectively (entries 9 and 10).

Table 1. Palladium- and Copper-Catalyzed Homocoupling of Organolead Compounds

Entry	Substrate	Method[a]	Product	Yield(%)[b]
1	**1a**	A	**3a**	68
2	**1a**	B	**3a**	68
3	**1b**	A	**3b**	65
4	**1b**	B	**3b**	62
5	**1c**	A	**3c**	75
6	**1c**	B	**3c**	80
7	**1d**	A	**3d**	81
8	**1d**	B	**3d**	78
9	**1e**	A	**4**	70
10	**1e**	B	**4**	53

[a] Method A: All the reactions were run in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) in $CHCl_3$ at room temperature for 10 min. Method B: All the reactions were run in the presence of CuI (10 mol %) in DMF at room temperature for 10 min. [b] The yields are isolated yields.

Experimental Section

Typical procedure.

Method A: Biphenyl (**3a**)

To a stirred solution of phenyllead triacetate (**1a**) (0.20 g, 0.43 mmol) in $CHCl_3$ (5 mL) was added $Pd_2(dba)_3{\cdot}CHCl_3$ (22.4 mg, 5 mol %) and the reaction mixture was stirred at room temperature for 10 min. After evaporation of the solvent, the crude product was separated by SiO_2 column chromatography (hexane Rf = 0.54) to afford biphenyl (**3a**) (22.7 mg, 68%). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39 (m, 2H), 7.47 (m, 4H), 7.62 (m, 4H). IR (KBr) 3205, 3099, 1602, 1466 cm^{-1}.

Method B:

To a stirred solution of phenyllead triacetate (**1a**) (0.20 g, 0.43 mmol) in DMF (4 mL) was added CuI (8.25 mg, 10 mol %) and the reaction mixture was stirred at 50 °C for 10 min. H_2O (20 mL) was added and extracted with ether (20 mL X 3). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by column chromatography (hexane, Rf = 0.54) to afford biphenyl (**3a**) (22.6 mg, 68%).

4, 4'-Dimethylbiphenyl (**3b**) TLC, SiO_2, hexanes, Rf = 0.51. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 6H), 7.24 (m, 4H), 7.47 (m, 4H). IR (KBr) 3107, 1452, 1368, 803, 720 cm^{-1}.

4, 4'-Dimethoxybiphenyl (**3c**) TLC, SiO_2, EtOAc : hexane = 1 : 30, Rf = 0.32. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.82 (s, 6H), 6.95 (m, 4H), 7.48 (m, 4H). IR (KBr) 3145, 1609, 1478, 1301, 1042 cm^{-1}.

2, 2'-Bithiophene (**3d**) TLC, SiO_2, hexanes, Rf = 0.52. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.99 (m, 2H), 7.17 (m, 4H). IR (KBr) 3081, 1783, 1372, 830, 695 cm^{-1}.

1, 4-Diphenylbutadiyne (**4**) TLC, SiO_2, hexanes, Rf = 0.43. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (m, 6H), 7.55 (m, 4H). IR (KBr) 3104, 2158, 1594, 1477, 920 cm^{-1}.

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